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ON THE WAVE-LIKE CHARACTER OF PERIODIC PRECIPITATES

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Received May 30, 1939

1. Introduction

The similarity between wave patterns and periodic precipitates was remarked upon nearly thirty years ago by St. Leduc.[1] The suggestion of a possible physical basis for such similarity is conveyed in Wo. Ostwald's " diffusion-wave " theory of the formation of the Liesegang precipitates ; in this theory, Ostwald[2] postulated the existence of three diffusion waves in the system corresponding to the external and internal electrolytes and the soluble product of the reaction. More recently the idea of a diffusion wave has been applied by Michaleff[3] and his co-workers in order to interpret an important feature of the observed pattern, namely, the widening of the space between the successive rings which corresponds with the slowing down of the diffusion occurring as we proceed outwards from the centre of the pattern. Christiansen[4] and Woulff have gone further and suggested a physical connection between the formation of the periodic precipitates and the De Broglie matter waves associated with the diffusing ion. Nikiforoff[5] and Kharamonenko find additional support for the wave idea in the observation that any point in the diffusion field can become the centre of a ring system ; they have made experiments which show that the front of a ring system is ' refracted ' in the optical sense when passing across the boundary between gels of different concentration.

When it is completely formed, a Liesegang pattern is a static structure and is therefore scarcely to be regarded as a wave phenomenon in the usual sense, as the latter involves a movement or periodicity in time. It may be permissible however to describe a periodic precipitate as a wave-like phenomenon, meaning thereby, that it presents some analogies in its spatial distribution to the configuration at a particular instant of a periodic train of waves. Even here a difficulty presents itself when we remember that in a periodic wave-train the disturbance may be either positive or negative whereas the density of a precipitate is of necessity a positive quantity. Indeed the essence of a wave is the fact just mentioned, namely, that its amplitude can have either sign, on which depends the possibility of the interference effects

which occur when superposed trains of waves reinforce or destroy each other. It is thus clear that the analogies between a wave and a periodic precipitate would be without physical content unless it can be shown by investigation that superposition effects can be observed in periodic precipitates analogous to interference and diffraction phenomena in acoustics and optics. Indeed, the existence of such superposition effects, if established, would enable the wave-like character of Liesegang precipitates to be regarded as an established fact besides giving it a real physical significance.

Three years ago, one of us (K. Subba Ramaiah) undertook systematic studies on periodic precipitates with a view to ascertain whether the particles in these precipitates had any specific crystal orientation. Observations made in the course of these studies by us in collaboration made it clear that superposition effects of the kind referred to in the preceding paragraph are actually exhibited by Liesegang precipitates, thus establishing their wave-like character. A general account of the observed phenomena and of their interpretation on the wave-hypothesis, together with the photographs illustrating the present paper, were laid before the Indian Academy of Sciences at Bangalore in a lecture delivered by the senior author on the 12th of November 1936. The hopes which were entertained of developing a mathematical theory of periodic precipitates on a wave-basis led to the printing of the lecture being deferred. The results were however included in the thesis for the doctorate submitted by K. Subba Ramaiah to the Madras University in October 1938. A preliminary note summarising them also appeared as a letter to *Nature* in its issue of August 20, 1938. Owing to various circumstances, it has not as yet been possible so far for either of us to devote much further attention to the subject. It has therefore been considered desirable to publish our work of 1936 substantially as presented in the Academy lecture of that year.

2. *Superposition of Wave-trains of Equal Amplitude*

In the theory of interference and diffraction phenomena, attention is usually paid only to the distribution of the intensity in the field, and not to the actual position of the wave-fronts in space at any given instant. This is natural, as the variation of intensity is the very essence of the theory of interference and in optical and acoustical phenomena is the feature accessible to direct observation. The configuration of the wave-fronts is indeed unobservable without special experimental aid, and the employment of stationary waves or alternatively of stroboscopic methods is necessary to reveal the position of the individual waves. In fact, the details of the wave-pattern in interference and diffraction phenomena are most readily grasped

by examining stroboscopic photographs of ripples on water or of ultra-sonic vibration within liquids. In relation to our present problem, the consideration of such features is even more important than that of intensity, for the reason that though the density of a precipitate may be qualitatively estimated or even quantitatively measured, it is a simpler matter to observe the geometric configuration of the precipitate. We shall therefore proceed to consider a few typical cases of superposition which, as we shall see presently, have an application to observable effects in periodic precipitates.

(i) *Two intersecting trains of the same wave-length and of the same amplitude.*—This is the typical case which shows in the clearest possible way how interference modifies the geometric configuration of a wave-pattern. If there were *no interference*, the wave-pattern at any instant would consist of two continuous and intersecting sets of parallel straight lines cutting each other obliquely and dividing the whole field into a net of similar rhombus-shaped figures, in the two pairs of parallel sides of which we recognise the two intersecting wave-trains. Interference completely alters this picture. We observe a pattern in which the two interfering wave-trains are no longer distinguishable, as these cohere with each other, forming wave-fronts which are everywhere parallel to the longer diagonal of the rhombus, while the lines of interference maxima and minima run parallel to the shorter diagonal, in other words perpendicularly to the direction of the resultant wave-fronts. It is important to notice that the wave-fronts are not continuous : the lines of maximum *positive* disturbance are to be found in each *alternate* rhombus, while the lines of maximum *negative* disturbance are to be found in the intervening ones, the two being separated by the *interference lines of zero amplitude*. In other words, if we consider only the waves of maximum positive displacement or only those of maximum negative displacement, *their fronts run discontinuously*, the interference lines of zero disturbance forming the terminations, and the wave-fronts on the other side of such interference line *being displaced by half a wave-length with respect to each other*. This is an effect very characteristic of interference, and taken together with the fact that the two separate sets of wave-fronts become indistinguishable is a complete demonstration of the wave-like nature of any phenomenon in which such features are noticed.

(ii) *Two intersecting trains of different wave-length and of equal amplitude.*—This case is very similar to the preceding one, except that the superposed wave-trains would form a net of parallelograms with unequal sides instead of rhombuses. The wave-fronts and interference lines would therefore be inclined to each other instead of being perpendicular. The wave-fronts would exhibit discontinuities similar to those already referred to in

the preceding case. Another new feature of the case now considered would be the secular movement of the interference lines in a direction parallel to themselves. This would give rise to the phenomenon of " beats " if we consider the variation of the disturbance at any point of space as a function of time. The wave-fronts as they move parallel to themselves and pass through any given point undergo periodic changes of amplitude, thus breaking up the disturbance into periodic groups. We are not however concerned with these secular aspects, if we confine attention to the form of the wave-pattern at a *particular instant.*

(iii) *Two parallel trains of unequal wave-length and of equal amplitude.*— In this case again, the two wave-trains (supposed to be of harmonic type) completely cohere and become indistinguishable, being replaced by a single train of intermediate wave-length which however is broken up into groups of waves separated by interference lines of zero-disturbance. The group-length is twice the distance between such successive interference lines, there being a sudden reversal in the phase of the resultant waves as we pass a line of zero disturbance. Half-way between the lines of zero intensity, we have the group maxima in which the amplitude of the individual waves is the sum of the amplitudes of the two superposed disturbances.

3. *Superposition of Wave-trains of Unequal Amplitude*

The results stated in the preceding section would be modified in a significant way if the superposed wave-trains are of unequal amplitudes. We shall consider first the typical case of two intersecting trains of the same wave-length. As the result of the inequality of the amplitudes, the interference minima will cease to be of zero amplitude, and the discontinuous changes of phase occurring at these minima must therefore disappear and be replaced by rapid but continuous changes of phase. The positions of the interference maxima and minima will however be unaltered as these are determined only by the relative phases of the two waves. We can easily indicate the changes to be expected in the forms of the wave-fronts by taking a case in which one of the interfering wave-trains is assumed to vanish and assuming its amplitude to be gradually increased to the full value, while that of the second wave-train is correspondingly diminished until it finally vanishes. It is obvious that in the two extreme cases when one or the other wave-train is non-existent, the resultant disturbance would have a continuous wave-front identical with that of the survivor. It follows that there would be continuity of wave-fronts also in the intermediate cases, such continuity being secured by a small rotation of the wave-fronts near the interference maxima accompanied by a marked curving round in the vicinity

of the interference minima, so that they join up continuously with the neighbouring wave-fronts on the other side of the minima. It is clear that when one of the interfering waves has a greater amplitude than the other, the resultant disturbance would follow more closely the outline of the stronger wave. The direction of the rotation and curvature of the wave-fronts must therefore undergo reversal when the stronger wave becomes the weaker, and *vice versa*. In the limiting case, therefore, when the waves are of nearly equal amplitude, we should have a bifurcation or forking consisting of very steeply inclined lines which connect up the wave-front more or less symmetrically with its two nearest neighbours on the other side of the interference minimum. This forking is replaced by a discontinuity of the wave-fronts when their amplitudes are exactly equal.

The features referred to above and deduced from general geometrical reasoning are readily to be noticed in any good photograph of interference effects with capillary waves on water or with ultra-sonic waves in liquids. Fig. 1 is a drawing made from a ripple photograph and exhibits clearly the

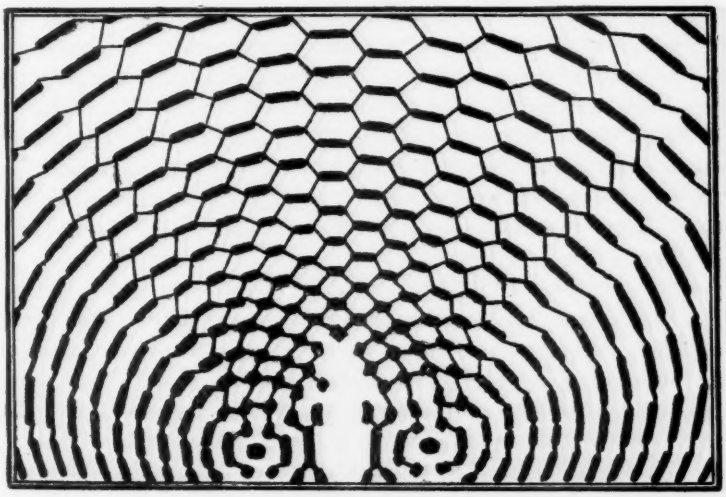

FIG. 1

Drawing from ripple photograph

effects mentioned. They may be explained in full detail by considering the configuration of disturbance as has been done by G. L. Datta[6] from whose paper the accompanying drawing of a small area of the central part of an interference field (Fig. 2) due to two similar centres of disturbance has been

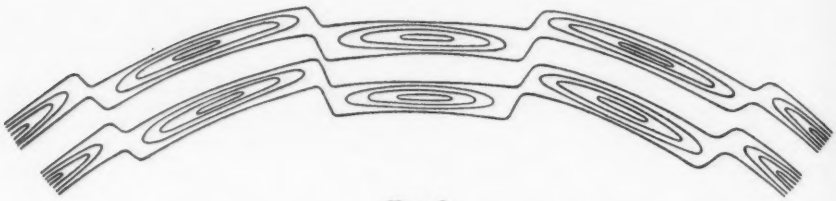

FIG. 2

Contours of equal amplitude

reproduced. The figure shows clearly the displacement of half a wave in the positions of the wave-fronts on either side of the interference lines, as well as the appearance of prongs or forks joining up these fronts. By drawing such figures for the case in which the amplitudes of the interfering waves differ greatly, we may illustrate the smaller and less abrupt changes of phase which then occur and the unsymmetrical curving of the wave-fronts which results therefrom, as may be seen in the outlying parts of the field in Fig. 1.

It is unnecessary to discuss in detail the case of two intersecting trains of unequal wave-length and unequal amplitude, as the features then to be expected would naturally be similar to those already discussed above. In the case of two parallel trains of unequal wave-length and of unequal amplitude, the groups of waves would no longer be separated by lines of zero disturbance with a discontinuous reversal of phase. We would have, instead, regions of maximum and minimum disturbance in which the wave-length, amplitude and phase all exhibit changes as we pass through different parts of the field. We shall not however consider these points in detail.

4. *Interference of Wave-groups*

If a source simultaneously emits two wave-trains of equal amplitude but of slightly different wave-length, the resulting disturbance would consist of a succession of wave-groups separated by regions of zero amplitude. If a second and similar source also emits such groups of waves and if the two trains traverse the field intersecting each other, it is clear that their superposition would give, besides the individual waves and groups emerging from the two sources separately, a further superposition effect, namely, two interference patterns corresponding to the two wave-lengths emitted by each of the sources separately. These interference patterns would be on different scales corresponding to the two different wave-lengths, and as these would again be superposed on each other, and as the phases of the wave-fronts change by a half period across each interference line, the result of such superposition would be a simple interference pattern corresponding to the mean

wave-length, and further overlying this we would have a " group interference pattern " in which the interference lines would run parallel to those in the " wave interference pattern " but would be much more widely spaced. This " group interference pattern ", which is here regarded as arising from the superposition of the two " wave interference patterns " may equally well be regarded as the result of the mutual interference of the two groups of waves emitted by the two sources separately. Such interference would be possible as the phase of each group as a whole reverses across each line of minimum disturbance in it. The two groups would thus tend to cancel each other's effects where their phases are opposite and to reinforce each other where they are in agreement. The length of the group being much greater than the length of the individual waves, the spacing of the interference lines in the group pattern would be correspondingly greater than the spacing of the interference lines in the wave pattern.

The discussion thus shows that when there are two similar sources emitting groups of waves, we have two kinds of interference pattern, one on a fine scale for the individual waves, and another on a much larger scale for the groups of waves. The two patterns would co-exist, but would be entirely separate and distinguishable. Further, we would also have the usual discontinuities of the wave-fronts in the wave interference patterns, and similar discontinuities of the group fronts in the group interference pattern but on a much larger scale. It should be remarked that the " group fronts " and the " wave-fronts " would everywhere run parallel. If, however, the discontinuities are replaced by continuous curves, forks or branches, the wave-fronts and group fronts would not be parallel to each other in the vicinity of the interference minima. The deviations from parallelism should be specially noticeable in the vicinity of the group interference minima, as these are on a relatively larger scale.

5. *Wave-interferences in Liesegang Patterns*

In the examples of rhythmic precipitation which illustrate the treatment of the subject in treatises on colloid chemistry and even in special monographs, we usually observe only a few unequally spaced bands of which the width is small compared with their mutual separation. The suggestion of a resemblance between such precipitates and the infinite train of harmonic waves postulated by the mathematician would seem indeed rather far-fetched. The case is however, different when we consider the rhythmic precipitates of silver chloride or silver phosphate in gelatin which are described more fully in the following paper. In these cases, we observe under the microscope thousands of rings following each other in regular succession,

and the width of the rings is everywhere comparable with their spacing. Such a periodic precipitate indeed strikingly suggests an analogy with an extended harmonic wave-train. The analogy becomes more specific if we compare the regions where the precipitate appears with the parts of the wave where the amplitude is positive and the empty spaces without deposit to the negative part.

Fig. 3 in Plate XX illustrates a small area in a rhythmic precipitate of silver chloride in gelatin, reproduced from a photomicrograph with a magnification of 160 diameters. In this area, we have a remarkably uniform and uninterrupted periodicity of the deposit. This however is the exception rather than the rule. Usually, even when the preparation is made with very careful technique, the rings exhibit non-uniformities of a very significant character, illustrations of some which are reproduced as Fig. 4 in Plate XX and Figs. 5 and 6 in Plate XXI. In Fig. 4, the interruption takes the form of a succession of forks running somewhat obliquely across the lines of the deposit near the centre of the field. A short distance away from this region of the forking, the lines of deposits become very sharp and straight and also much more intense than in the region of the forks. It will also be seen that the lines of deposit on the left side when produced correspond with the dark regions of no deposit on the right and *vice versa*. In the extreme left-hand top and the right-hand bottom corners, the forkings broaden giving rise to a distinct doubling of the lines of deposit. These features when considered together leave little doubt that we are here observing the effects of the " coherent interference " of two " periodic waves " of deposit of slightly different wave-length and direction and of nearly equal amplitude superposed on each other as discussed in Sections 2 and 3 of this paper.

Further confirmation of this view is furnished by Fig. 5. One of the effects indicated by the theory of interference is that when the area over which two intersecting wave-trains are superposed is sufficiently extended, we should observe a succession of equidistant interference lines running parallel to each other. Observation of the silver chloride precipitates shows that parallel and equidistant or nearly parallel and equidistant lines along which there is a sharp break or dislocation of the lines of precipitate occur so frequently as to exclude the possibility of their being accidental. Fig. 5 is an example of two such " interference lines " running parallel to each other and cutting across some thirty or more " waves " of the deposit, the wave-front exhibiting a sharp bend or a forking at each point of intersection.

Examination of silver chloride deposits shows that still another effect is common in them, namely, that of a succession of interference lines running

parallel to the wave-fronts, due evidently to parallel " waves of precipitation " of slightly different wave-length having been superposed. Fig. 6 is a photomicrograph of a portion of the field exhibiting such an effect. Over the greater part of the field, the two series of waves are " coherent " and form single sharp lines of heavy deposit, while in those regions where the waves are out of step, the deposits are relatively light. In the regions of light deposit, the individual waves and in the manner in which they fall out of phase can actually be observed in the distribution of the precipitate. Though this particular feature does not support the " interference " theory, it is not inconsistent with it, in view of the fact that the distribution of the precipitate is evidenly not of the simple harmonic type. Superposition of two waves which are not of harmonic type and which resemble periodic " pulses " would result in changes of form being observable in the vicinity of the intensity minima analogous to those actually seen in Fig. 6.

6. *Groups and Group-interferences in Rhythmic Precipitates*

The peculiar fine structure of periodic precipitates of silver chromate and the circumstances in which it is observable have been fully discussed in the following paper by one of us. The present trend of opinion appears to be that the so-called secondary structure of very finely spaced rings is due to presence of impurities in the gelatin leading to the formation of closely-spaced silver chloride or phosphate rings. Reasons have however been given in the following paper in support of the view that such impurity is probably not essential for the formation of secondary structure, the items of evidence being : (1) a thoroughly washed gelatin which shows only a slight turbidity but no rings with silver nitrate, produces both secondary and primary rings when pure potassium chromate is added to it ; (2) the spacing of the secondary silver chromate rings is not so close as that of the silver chloride rings ; and (3) the primary and secondary rings form a continuous periodic system observable everywhere in the field. An explanation has also been offered for the fact in certain circumstances the primary rings may be obtained without the secondaries being present.

A careful examination of the silver chromate rings in gelatin in various circumstances of formation reveals a variety of interesting effects, which fit beautifully into the theory of wave-interferences and group-interferences developed earlier in this paper. It should be remarked that this interpretation is wholly independent of any decision on the question whether or not the presence of a minute quantity of impurity in the gelatin is essential for the production of a periodic precipitate and on the question whether or not, such impurity plays an important part in the spacing and distribution of the

precipitate. We shall base ourselves solely on the observed facts regarding the configuration of the rings in various circumstances. Figs. 7 and 8 in Plate XXII, Figs. 9 and 10 in Plate XXIII and Figs. 11 and 12 in Plate XXIV are photomicrographs of small selected areas in silver chromate precipitates intended to illustrate the relationship between the so-called primary and secondary ring systems and the appearance of interference phenomena in them. Figs. 13 and 14 in Plate XXV, Fig. 15 in Plate XXVI and Fig. 16 in Plate XXVII are enlargements of the Liesegang patterns themselves; these are of the type from which selected areas have been enlarged and reproduced as Figs. 7–12. Figs. 13–16 are in fact intended to explain and illustrate the physical origin of the effects shown in Figs. 7–12. A careful study of the Plates shows that the configuration of the rhythmic precipitates is strikingly influenced by the initial geometrical distribution of the precipitating agent. In Fig. 13 we have a small circular drop of silver nitrate solution starting the precipitation; in Fig. 14 we have an elliptical drop, while in Fig. 15 we have two circular drops running into an oval figure; in Fig. 16 we have two separate drops separated by an interference dead space. Even in the case of the apparently circular drop illustrated in Fig. 13, we notice radial dislocations in the rings running outwards from the margin of the drop. The very striking perturbations of the rings seen in Fig. 14 with the elliptical drop indicate clearly that the form of its boundary is responsible for these effects. Further, in Figs. 15 and 16, the perturbations in the form of the rings are more prominent in the central regions where the effect of the two drops are superposed, and less prominent in the marginal areas where they are practically independent.

A study of the Liesegang patterns illustrated in Figs. 13 to 16 brings out the following interesting facts. Firstly, where the primary rings run most regularly, that is, without inflexions or changes of curvature, the secondary rings run most nearly parallel to the primaries; on the other hand, where the primaries bend round sharply, the secondaries tend to preserve their direction and therefore become inclined to the primaries. Secondly, when the primaries cut across a clear region or when they broaden out, the secondaries traversing them become very intense and are clearly seen, even though elsewhere in the clear regions they may be too feeble to be visible. Further, an examination of the patterns under a microscope shows that when the secondaries are at all visible, and irrespective of whether they are parallel or inclined to the primaries (see for instance, Figs. 7 and 8 in Plate XXII), the two systems run continuously into each other as part of a simple periodic distribution of precipitate. These three features together make it clear that the primary and secondary ring systems

are organically connected with each other and form part and parcel of a single phenomenon. It becomes therefore justifiable to regard the so-called primary rings as the groups, and the secondary rings as the waves of which the group is composed.

Figs. 9 and 10 in Plate XXIII are photomicrographs of a " group interference line". In Fig. 9 the secondaries are visible and sharply terminated by the interference line along which there is a discontinuous shift of half a group-length in the phase of the groups on either side of the minimum. On the other hand in Fig. 10, the secondaries are not visible and we have instead of a discontinuity, prongs or forks joining up the group maxima on either side of the interference line. It will be noticed that in Fig. 9 the disposition of the group maxima is quite symmetrical, while in Fig. 10 it is distinctly not so. Evidently in the latter case the interfering groups were not quite of equal amplitude.

Figs. 11 and 12 are intended to be a contrast to each other. Fig. 11 exhibits a " group-interference line " on either side of which the groups are discontinuous while the waves run continuously through. In Fig. 12 on the other hand, we see " a wave-interference line " crossing the whole field, including the intense primaries or wave groups and everywhere exhibiting a discontinuity in the phase of the secondaries or wave-fronts on either side of it. The groups as a whole, however, are entirely unaffected. Figs. 11 and 12 thus illustrate the fact that group-interference and wave-interference are two distinct phenomena, one on a large scale and the other on a fine scale.

7. *Origin of the Interference Effects*

It may be remarked that interference effects have also been observed with silver phosphate rings in gelatin, and with lead iodide rings in agar gels. In the former case, the effects are similar to those observed with silver chloride rings and in the latter they resemble those observed with the primary rings in silver chromate. These instances are sufficient to show that the phenomena we are considering are of a general nature. The question now arises how the actual interferences arise. From the facts already stated, we may infer that the effects owe their origin in the main to the irregular form of the boundary from which the diffusion starts, as the result of which we have two or more waves traversing the field simultaneously in different directions. It must be remembered that irregularities in the thickness of the gelatin film or in the concentration of the reacting materials present in it may also be responsible for the perturbations and result in interference or diffraction effects becoming observable in the field. It would obviously be desirable to make experiments in which pre-determined effects with rhythmic precipitates similar to the standard optical experiments in interference and

diffraction are produced by suitable technique. Some attempts in this direction were being made when the work was brought to a standstill by the departure of one of us from Bangalore. It is to be hoped that this experimental work as well as the theoretical interpretation of periodic precipitation on a wave-ba is will again receive attention from us at an early date.

Summary

It is pointed out that the suggestion of an analogy between periodic waves and rhythmic precipitation would be without physical significance unless it can be shown that the characteristic superposition effects observable with waves are also demonstrable with Liesegang patterns. Fourteen photomicrographs and enlargements of Liesegang precipitates of silver chloride and of silver chromate are reproduced with the paper which show that such superposition effects are actually to be observed, both in regard to the intensity of the deposits and in respect of their geometrical configuration. These examples illustrate the varying effects of the superposition of two wave-trains when their wave-length, direction and amplitude are individually or collectively different. It is shown theoretically that when groups of waves interfere, we have a group-interference pattern on a large scale in addition to a wave-interference pattern on a fine scale, the two being separate and distinguishable effects. It is observed that the so-called primary and secondary rings obtained with silver chromate precipitates in gelatin are related to each other as a group is to the individual waves of which it is composed. Independent wave-interferences and group-interferences are exhibited by such precipitates.

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4. Christiansen and Woulff *Zeit. Physik. Chem.*, 1934, **36 B**, 187.
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6. Datta .. "Sir Asutosh Mookerjee Commemoration Volume," *Science*, Calcutta University, 1921.

7. Photographs very clearly showing the dislocations in periodic precipitates appear in Suzanne Veil's monograph on *Les Periodicites De Structure*, Hermann & Cie, Paris, 1934, Plates I & II, and not so clearly in Hedges' *Liesegang Rings*, Chapman & Hall, London, 1932, Fig. 1. A beautiful example of a series of parallel dislocations is reproduced with a note by Dr. Liesegang in the *Zeitschrift fur Wissenschaftliche Mikroskopie and fur mikroskopische Technik*, 1936, Band **53**, p. 438, the photograph being by Manfred Köhn of Freiburg i. B. A reprint of the note was very kindly sent by Dr. Liesegang to Sir C. V. Raman in May 1939.

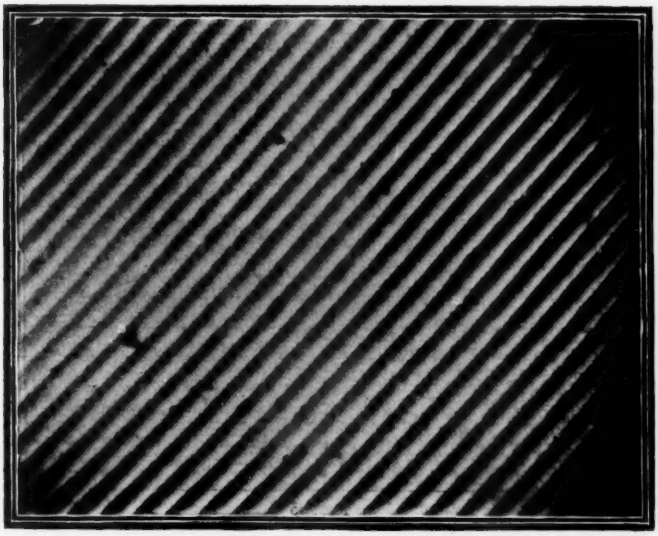

FIG. 3

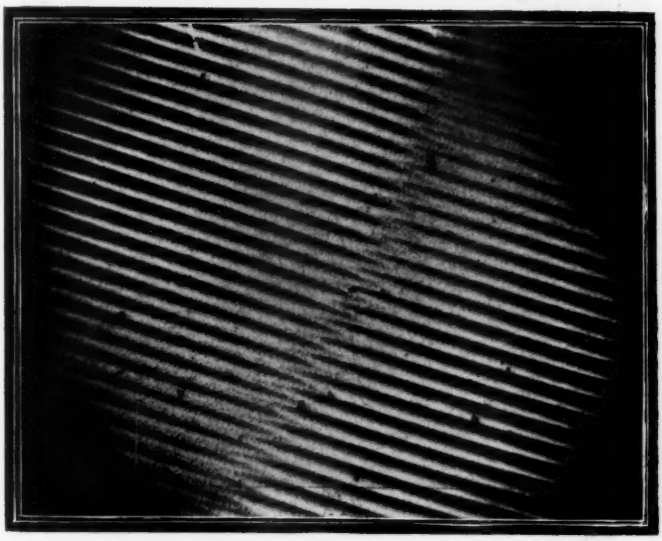

FIG. 4

FIG. 5

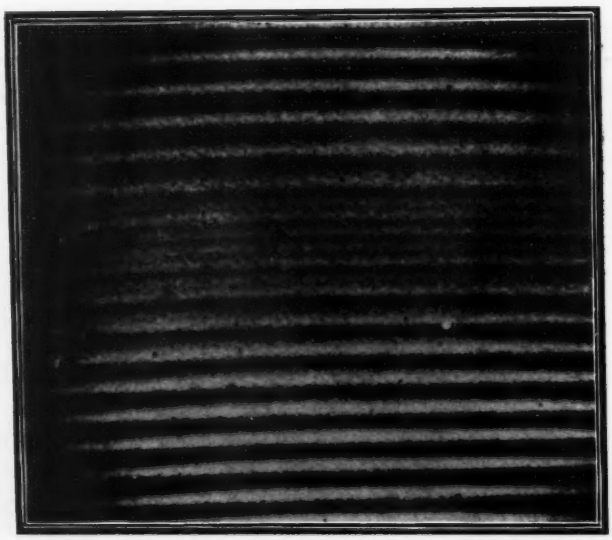

FIG. 6

FIG. 7

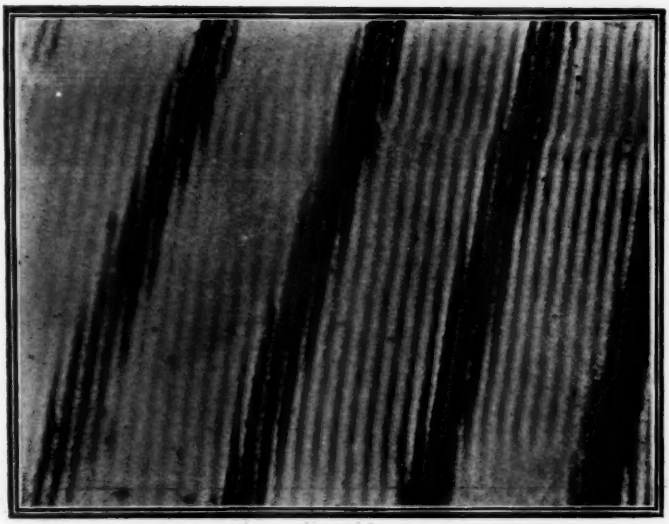

FIG. 8

FIG. 9

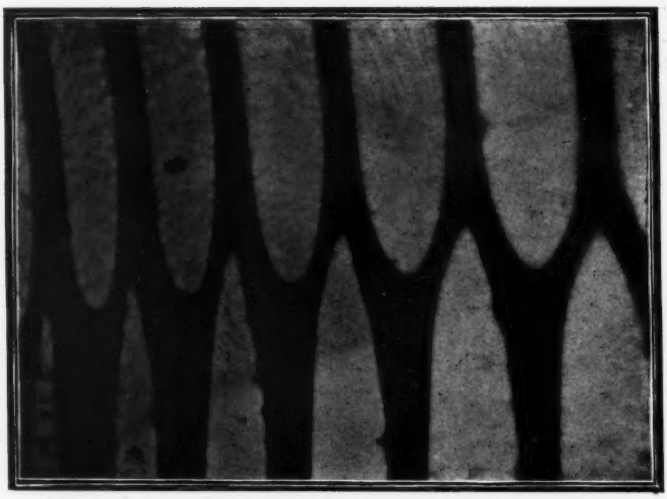

FIG. 10

FIG. 11

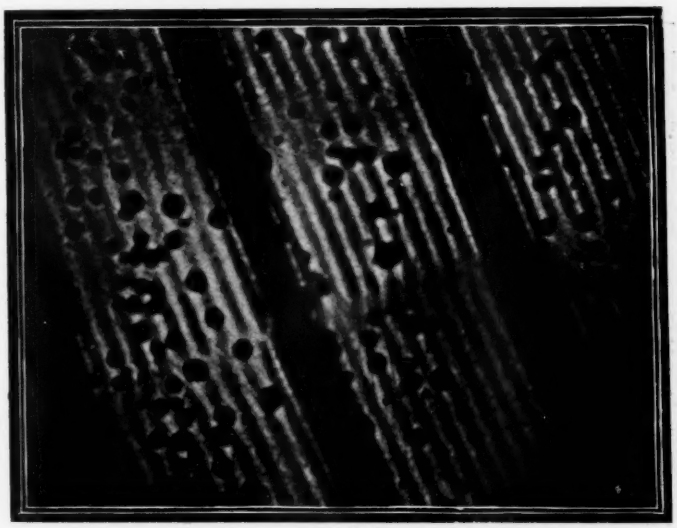

FIG. 12

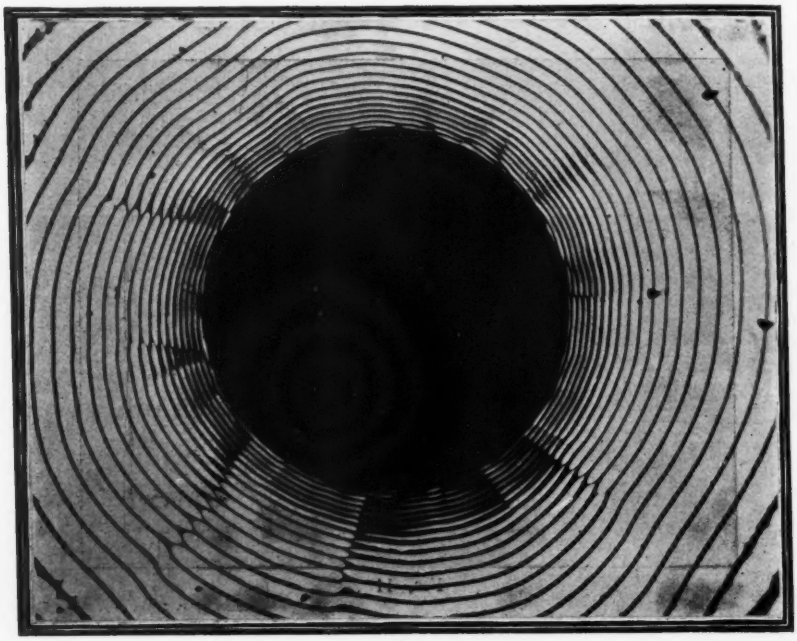

FIG. 13

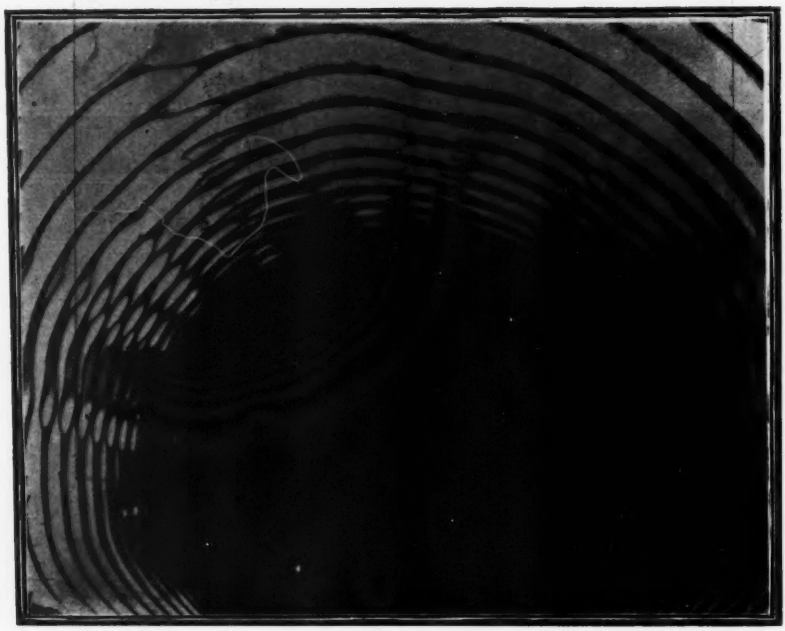

FIG. 14

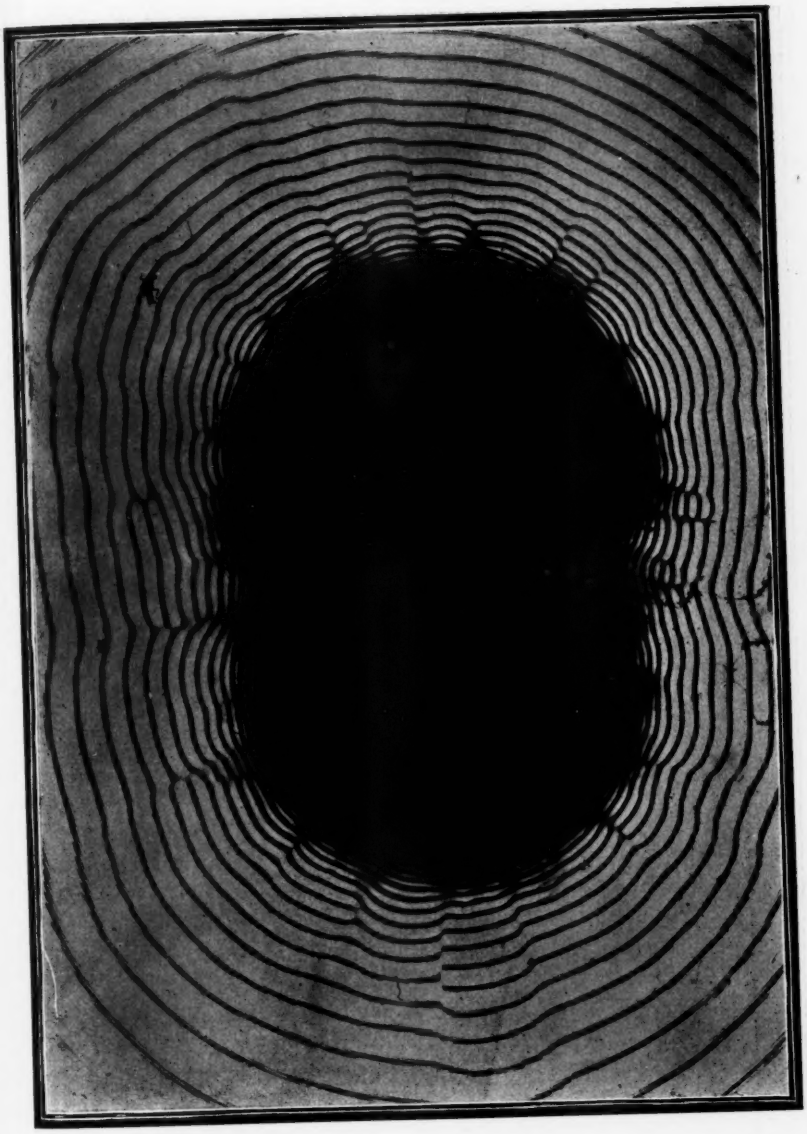

FIG. 15

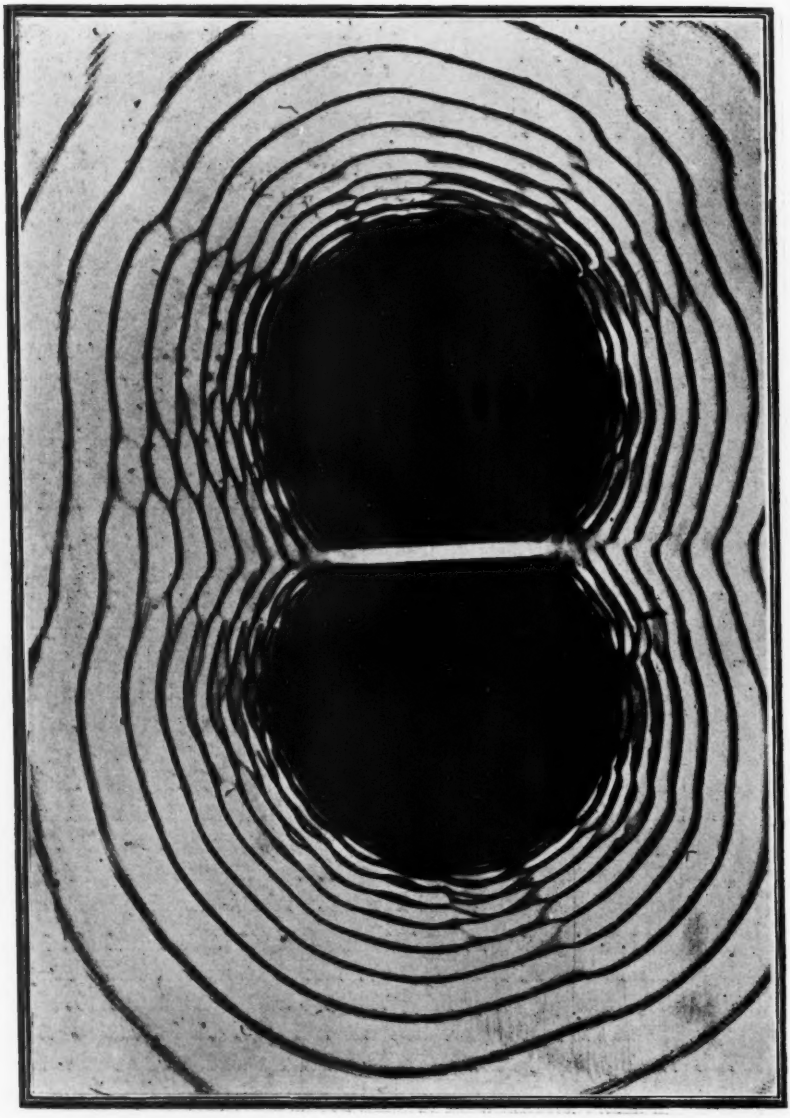

FIG. 16

STUDIES ON LIESEGANG RINGS

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Received May 31, 1939

1. Introduction

It has been widely recognised that a detailed study of the process of chemical reactions in gels is of importance particularly because many of the reactions in biological media and in geological systems are normally of this type. Among such processes, special interest is attached to the study of periodic structures initiated by Liesegang[1] over forty years ago. The complexity of the subject is, however, so great that in spite of the numerous contributions made year after year, the mechanism of the ring formation in the case of even such simple reactions as the precipitation of silver chromate in gelatin, is still obscure. In the course of an investigation on the nature and the mechanism of these ring formations, several interesting observations were made, which it is proposed to place on record here.

2. Experimental

(*a*) *Silver chloride rings in gelatin.*—The rings of extreme fineness produced by the diffusion of silver nitrate into a gelatin gel containing sodium chloride were first noticed by Moeller.[2] They were obtained in the following way. Good quality gelatin, of Kahlbaum's 'gold label' standard, was allowed to swell in water for a few hours, washed repeatedly and dispersed in nearly boiling water. It was then treated with a very small quantity of sodium chloride, filtered and poured on glass plates. After it had set, the gel was treated with a drop of concentrated silver nitrate solution and the plate was covered up to prevent the action of light. When next day the plate was examined, the precipitate of silver chloride formed was continuous to the naked eye but showed under the microscope thousands of very fine rings arranged in a regular order. The rings were very closely packed near the centre and more widely spaced at the edges, as many as 50–100 rings per millimeter being observed in the densely packed region. It was also noticed that the width of the rings was practically equal to that of the spacings separating them.

When two drops of silver nitrate were placed on the same plate, the pattern of the precipitate produced showed an interference dead space, which was absolutely free from the silver chloride rings.

Similar rings of silver chloride, visible only under high magnification, were also obtained in test tubes when silver nitrate diffused into a gelatin

gel containing a trace of sodium chloride. But in this case the rings were confined to a narrow region and bounded on either side by a continuous precipitate of the silver chloride.

Silver phosphate rings in gelatin were also obtained on glass plates in a similar manner by using sodium phosphate in place of sodium chloride. These rings were also very closely packed and showed a strong resemblance to the chloride rings in all their characteristics.

(*b*) *Silver chromate rings in gelatin.*—Silver chromate rings in gelatin were obtained on glass plates by the usual method of allowing silver nitrate to diffuse into a gelatin gel containing potassium chromate or dichromate. Only the purest chemicals were employed for this purpose and it was observed that the rings obtained with chromate were much closer and more numerous than those obtained with dichromate. This is quite in conformity with the observation made by Veil.[3] The ring systems were in most cases surrounded by a pale yellow fringe, as noticed by Friend[4] and others, the fringe being best pronounced at low concentrations of the potassium chromate. The spacings between the rings also showed on microscopic examination, large numbers of fine silver chromate particles.

The so-called ' secondary rings ' observed by Schleussner,[5] in the spacings between the ' primary rings ' were also clearly visible under the microscope. But a careful examination revealed some very interesting new features about them. These secondary rings are much finer and more closely spaced than the primary rings, while the latter also have a fine structure which is part and parcel of the secondary system. In other words, there is only one fundamental ring structure in the system consisting of fine rings. Superimposed on this is a second structure which can be conveniently termed as a periodic strengthening or intensification of the precipitate in these rings. The latter alone manifests itself to the naked eye in the form of ' primary rings'. In some cases, however, the intensification may be so great as to obscure the fine structure of the primary rings and thus create an illusion of discontinuity in the fundamental structure.

It is found that the two periodicities may be parallel to each other or may be inclined at an angle and this appears to be determined largely by the shape of the silver nitrate drop. The primary rings generally tend to conform to the outline of the drop but the secondary rings are more truly circular. This results in the two systems being inclined at an angle when the outline of the drop is somewhat irregular.

When two independent ring systems, produced by two drops of silver nitrate on the same plate interfered, no rings, either primary or secondary,

were found in the interference dead space. The primary rings of silver chromate were deformed but the secondary rings were in general circular and incomplete. This appears to suggest that the two periodicities might be due to independent, if also similar, causes. However a few cases were also observed in which the secondary rings exhibited deformation as well. It may also be mentioned here that the secondary rings generally started nearer the centre and ceased only after all the primary rings had been formed.

Previous investigators like Schleussner[4] have attributed the secondary rings to the presence of impurities in gelatin, like chlorides and phosphates. But it is difficult to reconcile this view with the existence of a continuous structure over the whole system. To confirm that the secondary rings were also due to silver chromate, experiments were carried out with pure gelatin which had been thoroughly washed to free it from chloride and phosphate impurities. This product when treated with a drop of silver nitrate solution gave rise to a very faint turbidity but did not show any rings. When mixed with potassium chromate, however, it successfully reproduced the primary and secondary rings of silver chromate.

It was noticed in the course of these experiments that the secondary rings were well developed only when the gelatin had set to a rigid gel before treatment with silver nitrate and also when the concentration of the chromate was within a narrow optimum range. When either of these conditions particularly the former, was not satisfied the secondary rings were found to be absent though the primary rings were often obtained. It is quite probable that the higher mobility of the particles in a loose gel does not favour the formation of closely spaced rings.

It is also necessary to point out that the secondary silver chromate rings were not as densely packed as those of silver chloride, and averaged about 20 rings per millimeter in the densest region. But as in the case of the chloride the width of these rings was equal to that of their intermediate spacings. The number of secondary rings between any two primary rings of a single system was also reasonably constant and was generally between the limits 7 and 10.

(*c*) *Lead iodide rings in agar agar.*—Lead iodide rings in agar agar were obtained, in plates as well as in test tubes, by allowing potassium iodide to diffuse into an agar gel impregnated with a suitable concentration of lead acetate. The rings were well defined and similar in their characteristics to the primary rings of silver chromate in gelatin. Microscopic examination however failed to show the existence of a secondary structure. The presence of crystals in the rings was easily perceptible and it was thought likely that they would show some definite orientation. They were therefore examined

between crossed nicols under a polarising microscope, but as the precipitation was too dense to transmit any light, no definite conclusions could be drawn. An X-ray examination of this and similar systems should however prove to be more fruitful and would be likely to throw further light on the mechanism of the ring formations.

(*d*) *Microphotometric examination of silver chromate rings in gelatin.*— With a view to examine further the nature of the multiple periodicity as also to study the nature and relative intensity of the precipitation in the secondary and primary rings, the glass plates containing silver chromate rings in gelatin were subjected to microphotometric examination. The only previous examination of this type is confined to the work of Veil.[3]

The microphotometer employed was of the Kipp and Zonen type, at a magnification of 50 diameters. A large number of systems were examined and the records obtained in five typical cases are shown in Figs. 1–5.

Fig. 1 refers to a system very similar to the one examined by Veil. It shows a large number (over twenty) of closely spaced primary rings, sharply

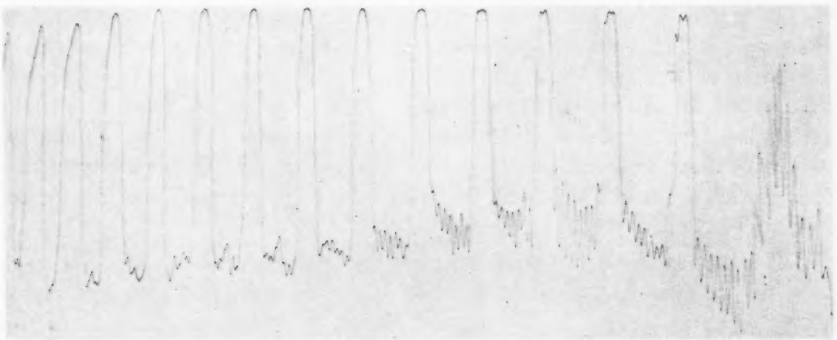

FIG. 1

defined and highly opaque. The spacing between successive rings increases only very gradually from the centre outwards. The secondary rings are very clearly defined in the outer regions. The fine structure is prominent only in the last primary ring and is either imperfect or totally absent in the others. The continuous nature of the fundamental ring system is clearly brought out in this as in all the other systems examined. The distribution of the precipitate in the rings is highly symmetrical but the intensity of the precipitate is considerably higher in the primary rings. The maximum opacity of all the primary rings, except the last, is nearly the same but in contradiction with Veil's observations the opacity of the drop region is found

to be slightly lower than the maximum opacity of these rings. The number of secondary rings in the region between any two primary rings is fairly constant and varies between 7 and 8.

Fig. 2 shows a smaller number of more widely separated primary rings. The fine structure of these rings is prominently seen in the earlier stages but

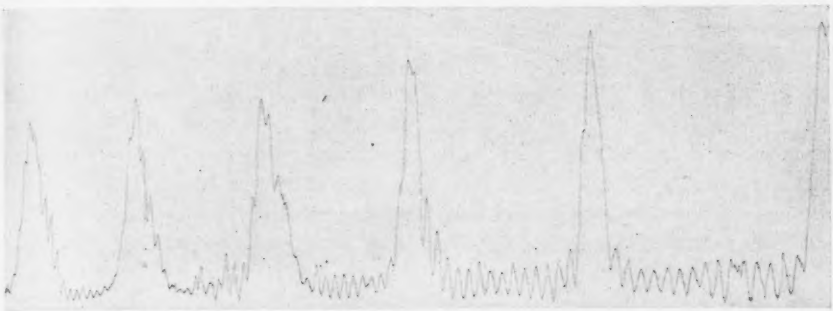

FIG. 2

shows a gradual falling off outwards. The maximum opacity of the primary rings as also the number of secondary rings in the intercepts between the primary, is not constant but increases from the centre towards the edges of the system. The distribution of the precipitate in the rings is symmetrical but the intensity is much larger in the primary than in the secondary rings.

Fig. 3 indicates a system obtained with potassium dichromate as against the chromate used in the previous cases. The rings are distinctly broader

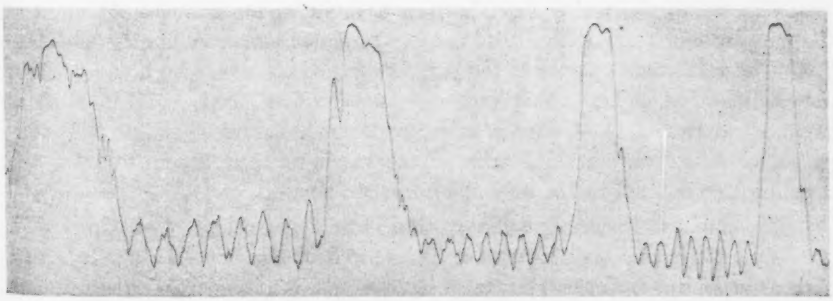

FIG. 3

and more widely spaced than in the other two cases. The fine structure of the primary rings is clearly visible through the entire region examined and the number of secondary rings in the intercepts is constant. The maximum

opacities of the primary rings are nearly the same and the distribution of the precipitate in the rings is also symmetrical. The intensity of the precipitation is considerably larger in the primary as compared with that in the secondary rings.

Figs. 4 and 5 also refer to systems obtained with potassium dichromate. The primary rings in both cases are very broad and diffuse. The curve in

FIG. 4

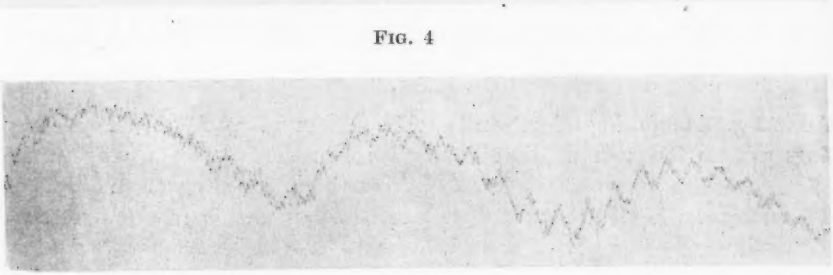

FIG. 5

Fig. 4 is nearly that of a sine showing a slight and continuous increase in the amplitude. The continuity of the fundamental structure is very conspicuous. The maximum opacity of the primary rings is not very high and whereas the distribution of the precipitate is symmetrical in Fig. 4, it is slightly asymetrical in Fig. 5. Under a microscope both systems showed numerous grains of silver chromate distributed at random, thus accounting for the irregularities noticed in the microphotometric curves.

The contrast between the sharp and closely spaced rings obtained with potassium chromate and the broad, diffuse and widely spaced rings obtained with dichromate, is very striking. The precipitation intensity in the primary rings is also very much higher in the former case. In general however the examination establishes the continuity of the fundamental ring structure. The precipitation in the rings is symmetrical about the centre and the number of secondary rings occurring in the spacings between the primary rings is constant.

(*e*) *The spacing in Liesegang rings.*—The spacing between successive rings in a Liesegang system is known to increase (except in a few well-known cases) with increasing distance from the diffusion centre. The spacing is generally a function of various factors such as the concentrations of the reacting electrolytes, the nature and the concentration of the gel medium, the temperature, etc. A certain regularity in the variation of the spacings is however claimed to have been observed by several investigators. Schleussner[6] found that the radii of the rings form a simple geometric progression. Veil[3] on the other hand found that the square roots of the intercepts between successive rings form an arithmetic series. Other formulæ have been suggested by Jablezynski and Kobryner[7] and others taking into account the time interval between the formation of successive rings. The laws of Jeblezynski and Veil are also claimed to have been inferred from an analogy between Leisegang rings and the De Broglie matter waves put forward by Michaleff and his co-workers.[8]

To verify the laws of Schleussner and Veil, the radii of the rings were measured in a number of systems of silver chromate rings in gelatin and lead iodide in agar agar. In the former case attention was confined only to the primary rings but the conclusions can be applied equally to the secondary rings as well. The measurements were carried out with a travelling microscope.

The results obtained with two systems of each type of rings are shown graphically in Figs. 6–9. These figures show respectively (1) the radii of the rings ; (2) the square roots of the rings ; (3) the logarithms of the radii of the rings (Schleussner's law) and (4) the square roots of the intercepts between successive rings (Veil's law), plotted against the numerical order of the rings. Curves A and B in the figures refer to the rings of silver chromate and C and D to those of lead iodide.

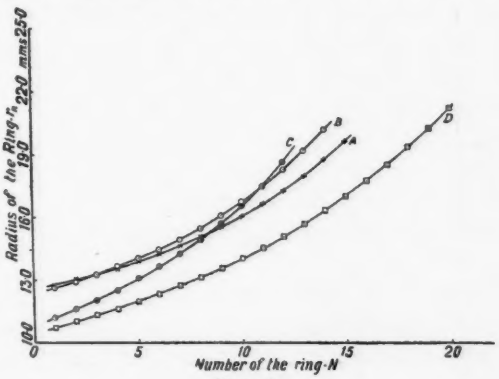

FIG. 6

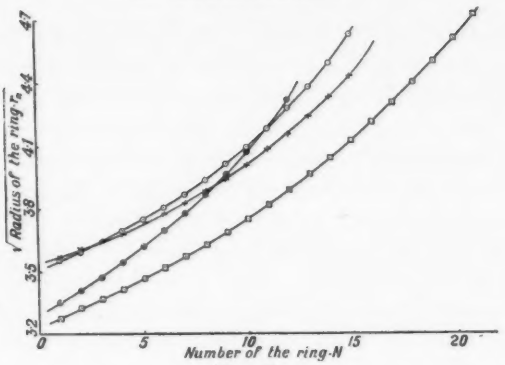

FIG. 7

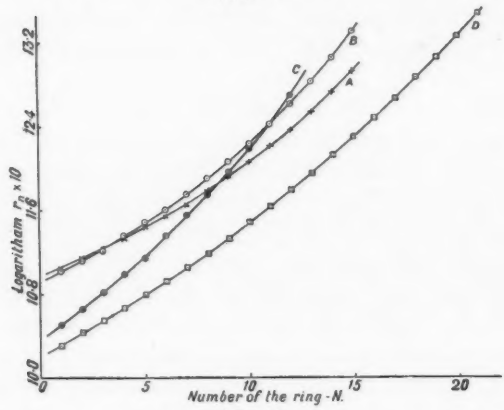

FIG. 8

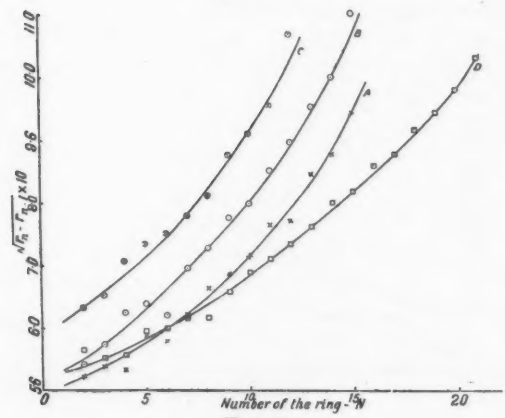

FIG. 9

The results indicate that in all the cases examined, the law of Veil does not hold over the whole range. Schleussner's law appears to be a better approximation to observed facts but even here the agreement is not too close. Of the four simple functions of the radii examined, the variation is linear in all cases over a small range but not over the entire range. The closest approach to linearity is obtained in the case of the logarithms of the radii. It is therefore difficult to draw any general conclusions about the actual manner in which the spacings betwen successive rings vary but it can be pointed out that this variation is perfectly gradual and regular and probably cannot be expressed as a simple function of the radii of the rings.

(*f*) *Some optical phenomena in Liesegang rings* : *Diffraction Spectra.*—A point source of white light when viewed through a glass plate containing silver chromate rings in gelatin showed beautiful diffraction spectra of 3 to 4 orders or even more. These spectra were very clear and widely separated from each other and were evidently due to the secondary rings of silver chromate acting in the nature of a diffraction grating. The separation between the different orders gradually diminished as the eye travelled away from the centre of the system. Also the spectra on the two sides were not identical, those nearer the centre showing a larger mutual separation.

In some cases where the primary silver chromate rings were sufficiently close to each other (one or more rings per mm.) a careful examination revealed the presence of a second series of diffraction spectra similar to the first but with considerably smaller mutual separation.

Silver chloride and silver phosphate rings in gelatin showed only one series of diffraction spectra similar to those caused by the secondary silver chromate rings but with even larger separations between the different orders. In several cases these spectra were conveniently employed to locate the regions where the rings were present.

(*g*) *Coloured haloes.*—It was often observed that well-defined silver chromate ring systems were surrounded by one or more circular coloured haloes exhibiting all the spectral colours. These haloes appeared near the edges of the ring system, coming one immediately after the other. The first halo or the one nearest to the centre was the most intensely coloured and the intensity was considerably smaller in the second and third. The colours were best seen in transmitted light and red was invaribaly found to be on the inside of these haloes.

In those cases where the silver chromate rings were ill-defined due to any cause whatsoever, the haloes were generally absent. The outline of the haloes in all cases followed that of the secondary and not the primary rings.

In no case were the haloes seen beyond the pale yellow fringe surrounding the ring system. The size of the haloes was variable depending on the angle at which the plate was held and was maximum when the plate came directly between the eye and the source of light.

Haloes were also observed in silver chloride and silver phosphate rings and were very similar to those in silver chromate. In cases where the silver chloride had formed a continuous precipitate the haloes were totally absent.

It is clear that these haloes are not due to the diffraction of light by silver chloride or secondary silver chromate rings because they are quite distinct from the diffraction spectra described earlier and are often seen in regions where the fine rings have ceased to exist. Also they are seen at far larger angles than is theoretically possible in the case of diffraction. Microscopic examination of the halo region however showed the existence of numerous fine particles of the silver salts arranged in a more or less regular manner, the smallest particles being nearest to the centre. It was also observed in this connection that the colours of the haloes by scattered light were considerably weaker but complementary to those seen in transmitted light. It is probable therefore that the haloes are due in some way to the diffraction of light by the fine precipitate particles formed outside the ring region but the problem requires further investigation. The possibility of the colours being analogous to those of mixed plates should also be borne in mind.

(*h*) *Colours of silver chloride rings.*—It was seen that in many cases the silver chloride ring systems in gelatin exhibited different colours at different points. In one typical case, in transmitted light, there was seen to be a central colourless and transparent zone corresponding to the region of the silver nitrate drop. This was surrounded by a faint brick red region followed by another fainter region of the same colour. Later appeared a broad violet coloured band surrounded finally by a white zone. Colours of the complementary order were seen in the light scattered by the system. This phenomenon was quite distinct from that of the coloured haloes and was evidently due to a continuous variation of the size of the precipitated particles in the rings themselves. The existence of this variation was confirmed by microscopic examination under very high magnification, when the particle size was found to increase gradually from the centre outwards. Similar colour effects, but in a less striking degree, were observed when the silver chloride rings were formed in test tubes instead of on plates.

3. *Discussion*

It had so far been assumed by colloid chemists that the fine rings present in the spacings between primary rings of silver chromate in gelatin were

caused by the presence of impurities in the gel. Foster[9] had also pointed out that the presence of chloride impurities causes the silver chromate rings to occur in groups of three instead of singly. But the observations recorded in this paper indicate that both views are incorrect. The existence of a continuous structure of fine rings in the system coupled with the fine structure of the primary rings themselves definitely indicates the presence of a double periodicity, the first of which causes the fomation of fine silver chromate rings and the other, superposed on it, causes a periodic intensification of the precipitate in these rings. The origin of the multiple periodicity is, however, difficult to explain but it is very probable that similar if not identical forces are responsible for their existence. This is particularly borne out by the fact that the inclination of the two periodicities to each other is largely governed by the shape of the silver nitrate drop. Any comprehensive theory of the Liesegang phenomenon that may be put forward must be able to satisfactorily explain this phenomenon of multiple periodicity.

The very fine rings of silver chloride and silver phosphate in precipitated gelatin do not exhibit a double periodicity and as such form very convenient media for studies on the mechanism of the Liesgang ring formations.

The microphotometric examination of silver chromate rings in gelatin has confirmed the existence of a double periodicity in that system. It has also thrown light on the various types of chromate rings that are generally formed and on the different ways in which the precipitate may be distributed between the primary and the secondary rings.

Observations have also been made on some striking optical effects seen in Liesegang rings. Stress may be laid on the beautiful spectra of several orders formed when the rings act as a diffraction grating and on the colours exhibited by silver chloride rings due to variations in the particle size of the precipitate. The explanation of the formation of coloured haloes is however not very simple and requires further investigation.

In conclusion, the author expresses his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his very keen and helpful interest in this work.

4. Summary

Microscopic and microphotometric examinations of silver chromate rings in gelatin have established the existence of a double periodicity in that system. One of these causes the formation of a continuous structure of fine microscopic rings and the other causes a periodic intensification of the precipitate in them. The latter of the two manifests itself to the naked eye as the ordinary rings of silver chromate. It has also been shown that the fine

rings consist of silver chromate and are not due to the presence of impurities in the gelatin.

Differences have been observed between systems in which potassium chromate and potassium dichromate have been employed in the reaction. The primary rings obtained in the former case are numerous, sharp, closely spaced and highly opaque whereas in the latter they are broad, diffuse and more widely spaced. The distribution of the precipitate in both cases is, in general, symmetrical about the centre in the primary as well as the secondary rings.

Measurements of the radii of rings of silver chromate in gelatin and lead iodide in agar agar have shown that the laws of Schleussner and Veil are not strictly true over a large range. The variation in spacing is however gradual and regular and is probably not a simple function of the radii of the rings.

It has been experimentally demonstrated that under suitable conditions, the precipitation of silver chloride and silver phosphate in gelatin is a periodic and not a continuous process and gives rise to a series of extremely fine rings. As these rings do not show any multiple periodicity they form valuable media for studies on the mechanism of the Liesegang ring formations.

Some interesting optical effects exhibited by the rings have also been studied. The closely spaced rings in the silver chromate, chloride and phosphate systems can act as a diffraction grating and give rise to a series of beautiful diffraction spectra. The variation of the grain size of the precipitate in silver chloride rings causes the system to exhibit different colours in different regions. Attention is also drawn to the existence of beautiful coloured haloes in many of the systems examined.

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ON NON-LINEAR PARTIAL DIFFERENTIAL EQUATIONS OF THE PARABOLIC TYPE

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Introduction

1. The present paper is devoted to the study of some boundary value problems in the theory of non-linear partial differential equations of the parabolic type in their normal form. Consider, for example, the non-linear equation

$$\frac{\partial}{\partial x}\left(\rho\,(x)\,\frac{\partial u}{\partial x}\right)-\frac{\partial u}{\partial t}=f\,(x,\,t,\,u,\,p),\;p=\frac{\partial u}{\partial x} \tag{1}$$

for the boundary conditions

$$u\,(0,\,t)\;=u\,(\pi,\,t)\;=0\,;\,t\geqslant 0\qquad u\,(x,\,0)=u_0\,(x) \tag{2·1}$$

$$u\,(0,\,t)\;=\frac{\partial u}{\partial x}\,(\pi,\,t)=0\,;\,t\geqslant 0\qquad u\,(x,\,0)=u_0\,(x) \tag{2·2}$$

$$\frac{\partial u}{\partial x}\,(0,\,t)=\frac{\partial u}{\partial x}\,(\pi,\,t)=0\,;\,t\geqslant 0\qquad u\,(x,\,0)=u_0\,(x) \tag{2·3}$$

$$\begin{cases}u\,(0,\,t)=u\,(\pi,\,t)\\ \rho\,(0)\,\dfrac{\partial u}{\partial x}\,(0,\,t)=\dfrac{\partial u}{\partial x}\,(\pi,\,t)\,\rho\,(\pi)\end{cases}\qquad t\geqslant 0\qquad u\,(x,\,0)=u_0(x) \tag{2·4}$$

where $\rho\,(x)$ is an essentially positive function continuous and bounded together with its first and second derivatives in $0\leqslant x\leqslant\pi$. Applying the method of separation of variables we shall solve (1) in the form

$$u\,(x,\,t)\;=\Sigma\,u_n\,(t)\,\phi_n\,(x) \tag{3}$$

so that

$$u\,(x,\,0)\;=u_0\,(x)\;=\Sigma\,c_n\,\phi_n\,(x),\;\;c_n\;=u_n\,(0) \tag{4}$$

where $\phi_n\,(x)$ are the complete normal orthogonal eigen-functions of the associated Sturm-Liouville differential equation

$$\frac{d}{dx}\left(\rho\,\frac{d\phi}{dx}\right)+\lambda\,\phi\;=0 \tag{5}$$

for the corresponding boundary conditions

$$(6\cdot1) \qquad \phi\ (0) = \phi\ (\pi) = 0$$

$$(6\cdot2) \qquad \phi\ (0) = \phi'\ (\pi) = 0$$

$$(6\cdot3) \qquad \phi'\ (0) = \phi'\ (\pi) = 0$$

$$(6\cdot4) \qquad \phi\ (0) = \phi\ (\pi)\ ;\ \phi'\ (0)\ \rho\ (0) = \phi'\ (\pi)\ \rho\ (\pi).$$

We shall denote by λ_n the eigen-value corresponding to $\phi_n(x)$. In the case of the boundary conditions $(2\cdot1)$ and $(2\cdot2)$ it was shown by Dr. M. R. Siddiqi[1] that if $f(x, t, u, p)$ can be developed in a series of the form $\sum_{r,s}^{1\cdots\infty} p_{r,s}(x,t)\, u^r p^s$, there exists one and only one solution of (1) in the form (3) such that for all values of t, the series $\Sigma\ \lambda_n^{\frac{3}{2}}\ u_n(t)$ is uniformly and absolutely convergent, provided $\Sigma\ \lambda_n^{\frac{3}{2}}\ |c_n| = c$ is sufficiently small. His method can be applied to the boundary conditions $(2\cdot3)$ and $(2\cdot4)$ and it can be shown[2] that if c is small and if $t < A(c)$, where A is a constant depending on c there exists one and only one solution of (1) in the form (3) so that the series $\Sigma\ \lambda_n^{\frac{3}{2}}\ u_n(t)$ is absolutely and uniformly convergent. The difference in result is due to the fact that $\lambda_0 = 0$ is an eigen-value with a corresponding non-vanishing eigen-function $\phi_0(x) = \frac{1}{\sqrt{\pi}}$ in the case of these boundary conditions.

1·1 But in this paper the same problem is studied with more general hypotheses on $f(x, t, u, p)$. Using some elementary theorems as the Reisz-Fischer theorem on the expansion of an arbitrary function in Sturm-Liouville eigen-functions, we solve the system of non-linear integral equations that arise by the method developed by the author in a previous paper.[3] In fact it is shown that if $\Sigma\ \lambda_n\ c_n^2$ is convergent and if $f(x, t, u, p)$ is defined $0 \leqslant x \leqslant \pi$, $t \geqslant 0$ and all real values of u and p, is continuous with respect to all the variables and is Lipschitzian with respect to k and p, in addition to satisfying the boundary conditions with regard to x, we can solve (1) uniquely in the form (3) such that the series $\Sigma\ \lambda_n\ u_n^2$ is uniformly convergent in any finite interval (O T). If $f(x, t, u, p)$ has bounded partial derivatives f_x', f_u', f_p' which are continuous and if $\Sigma\ \lambda_n^2\ c_n^2$ is convergent it is shown that $\Sigma\ \lambda_n^2\ u_n^2$

[1] " Sur la theorie des equations non-lineaires aux derivees partielles," *Comptes Rendus*, 1936, **203**, 1120.

[2] See my paper " On the Theory of Non-Linear Partial Differential Equations of the Parabolic Type," *Jour. Ind. Math. Soc.*, 1939, **3**.

[3] " On an Infinite System of Non-linear Integral Equations," *Proc. Ind. Acad. Sci.*, 1938, **8**, 238.

will be uniformly convergent in (O T). If $\Sigma\ \lambda_n^3\, c_n^2$ is convergent and if f has bounded partial derivatives of second order with respect to x, u and p $\Sigma\ \lambda_n\, u_n$ will be absolutely and uniformly convergent in (O T). If f is defined not for all real values of u and p but for $-\mathrm{N} \leqslant u, p \leqslant \mathrm{N}$ but otherwise satisfies the previous conditions, the solution is possible for small values of t. In later sections we study systems of equations and equations in more than two independent variables.

Preliminaries

2. We shall first enunciate certain properties of the Sturm-Liouville eigen-functions of (5) which will be frequently required.

2·1. It is well known[4] that there exists an infinity of eigen-values λ_n, arranged in increasing order of magnitude with the corresponding eigen-functions $\phi_n(x)$ which are complete normal, orthogonal and bounded. We further observe that the eigen-values λ_n of (5) for the boundary conditions (6) are all non-negative, for if λ is an eigen-value with $\phi(x)$ as the corresponding eigen-function

$$\lambda = \lambda \int_0^\pi \phi^2(x)\, dx = -\frac{\lambda}{\lambda} \int_0^\pi \phi\, (\rho\, \phi')'\, dx \tag{7}$$

$$= -[\phi\, \rho\, \phi']_0^\pi + \int_0^\pi \rho\, \phi'^2\, dx.$$

The first expression on the right vanishes on account of the boundary conditions and the second term is positive except when $\phi'(x) \equiv 0$, that is when $\phi(x) \equiv$ constant. In the case of the first two boundary conditions (6·1) and (6·2) $\phi(x) \equiv 0$ which is trivial, while in the next two (6·3) and (6·4) $\phi(x) = \frac{1}{\sqrt{\pi}}$ since ϕ is normal.

Thus in the first two cases of the boundary value problems all the eigen-values are positive, while in the next two $\lambda = 0$ is an eigen-value with the non-vanishing eigen-function $\phi(x) = \frac{1}{\sqrt{\pi}}$, the others being positive.

2·2. Secondly, it may be noted that in all these cases the functions

$$\psi_m(x) = \frac{\sqrt{\rho(x)}}{\sqrt{\lambda_m}}\, \phi_m'(x) \tag{8}$$

the positive sign of the radicals being taken, form a normal orthogonal set.

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[4] Courant, R., und Hilbert, D., *Methoden Der Mathematischen Physik*, Erster Band, 2nd Ed., p. 251.

For

$$(9)\qquad \int_0^\pi \psi_m(x)\,\psi_n(x)\,dx = \frac{1}{\sqrt{\lambda_m}\sqrt{\lambda_n}}\int_0^\pi \rho(x)\,\phi_m'(x)\,\phi_n'(x)\,dx$$

$$= \left[\frac{\rho(x)\,\phi_m\,\phi_n'}{\sqrt{\lambda_m}\sqrt{\lambda_n}}\right]_0^\pi - \frac{1}{\sqrt{\lambda_m}\sqrt{\lambda_n}}\int_0^\pi \phi_m\,(\rho\,\phi_n')'\,dx$$

$$= \sqrt{\frac{\lambda_n}{\lambda_m}}\int_0^\pi \phi_m\,\phi_n\,dx$$

$$= \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n. \end{cases}$$

The question arises whether they are complete. They need not be complete as can be seen from circular functions. However we can show that the functions $\psi_m(x)$ are complete with respect to all integrable functions $f(x)$ such that $\phi(x) = \int_0^x f(t)\,dt$ satisfies the boundary conditions. If there were to exist a function $f(x)$ satisfying the above conditions and such that

$$(10)\qquad \int_0^\pi \sqrt{\rho(x)}\,f(x)\,\psi_m(x)\,dx = 0 \text{ for every } m = 1, 2, \cdots$$

then

$$\int_0^\pi \sqrt{\rho}\,f\,\psi_n\,dx = \frac{1}{\sqrt{\lambda_m}}\int_0^\pi \rho f\,\phi_m'\,dx$$

$$= \left[\frac{\rho\,\phi_m'\,\phi}{\sqrt{\lambda_m}}\right]_0^\pi - \frac{1}{\sqrt{\lambda_m}}\int_0^\pi \phi(x)\,(\rho\,\phi_m')'\,dx$$

$$= \sqrt{\lambda_m}\int_0^\pi \phi(x)\,\phi_m(x)\,dx$$

$$= 0 \text{ for every } m.$$

This implies that $\phi(x) \equiv 0$, which means to say that $f(x) = \phi'(x) \equiv 0$ and our statement is proved.

2·3. The asymptotic values of $\phi_n(x)$ and λ_n are known[5] and we remain content with stating that $\phi_n(x)$ are uniformly bounded in $(0\ \pi)$ and that $\lambda_n = 0(n^2)$ so that $\sum_{n:1}^{\infty} \lambda_n^{-1}$ is convergent.

2·4. Finally we make a few remarks on the expansion of an arbitrary function in Sturm-Liouville eigen-functions. Let $\phi(x)$ be an arbitrary

[5] Ince, *Ordinary Differential Equations*, p. 270.

function integrable L^2 satisfying the boundary conditions then

$$\phi(x) \sim \Sigma c_n \phi_n(x), \quad c_n = \int_0^\pi \phi(x)\,\phi_n(x)\,dx \tag{11}$$

and by the known Reisz-Fischer theorem

$$\int_0^\pi \phi^2(x)\,dx = \Sigma c_n^2. \tag{12}$$

Let us now suppose that $\phi(x)$ is the integral of an L^2 function $\phi'(x)$ and that $\phi(x)$ satisfies the boundary conditions, then

$$\sqrt{\lambda_n}\, c_n = \sqrt{\lambda_n} \int_0^\pi \phi(x)\,\phi_n(x)\,dx$$

$$= \int_0^\pi \sqrt{\rho(x)}\,\phi'(x)\,\psi_n(x)\,dx.$$

Now we can apply Reisz-Fischer theorem as ψ_m's are closed with respect to functions $\phi'(x)$, so that

$$\int_0^\pi \rho\,\phi'^2\,dx = \Sigma \lambda_n c_n^2. \tag{13}$$

If further $\phi'(x)$ is the integral of an L^2 function $\phi''(x)$, then

$$c_n = \int_0^\pi \phi(x)\,\phi_n(x)\,dx$$

$$= -\frac{1}{\lambda_n} \int_0^\pi \phi\,(\rho\,\phi_n')'\,dx$$

$$= -\frac{1}{\lambda_n} \int_0^\pi (\rho\,\phi')'\,\phi_n\,dx.$$

Thus

$$\int_0^\pi (\rho\,\phi')'\,\phi_n\,dx = -\lambda_n c_n$$

so that

$$\int_0^\pi \{(\rho\,\phi')'\}^2\,dx = \Sigma \lambda_n^2\, c_n^2. \tag{14}$$

More generally if $\phi^r(x)$ exists and is integrable L^2 it can be shown that the series $\Sigma \lambda_n^r c_n^2$ is convergent where r is an integer.

The Non-Linear Equation in its Normal Form.[6]

3. Now consider the non-linear partial differential equation

$$\frac{\partial}{\partial x}\left(\rho \frac{\partial u}{\partial x}\right) - \frac{\partial u}{\partial t} = f(x, t, u, p), \quad p = \frac{\partial u}{\partial x} \tag{1}$$

for the boundary conditions

$$u(0, t) = u(\pi, t) = 0, \qquad t \geqslant 0 \tag{2·1}$$

$$u(x, 0) = u_0(x) \sim \Sigma c_n \phi_n(x) \tag{4}$$

where $\phi_n(x)$ are the eigen-functions of

$$(\rho\phi')' + \lambda\phi = 0 \tag{5}$$

$$\phi(0) = \phi(\pi) = 0 \tag{6·1}$$

with the corresponding eigen-values λ_n. We shall find a solution of (1) in the form

$$u(x, t) \sim \sum_{n=1}^{\infty} u_n(t)\, \phi_n(x). \tag{3}$$

We assume the possibility of expanding $f(x, t, u, p)$ in a series of Sturm-Liouville eigen-functions $\phi_n(x)$. A necessary condition is that f satisfies the boundary conditions (2·1) that is

$$f(0, t, 0, p_0) = f(\pi, t, u, 0, p_\pi) = 0.$$

So it is sufficient if $f(x, t, u, p)$ is continuous with respect to all the variables and

$$f(0, t, 0, \alpha) = f(\pi, t, 0, \alpha) = 0 \tag{15}$$

for all real α and all $t \geqslant 0$. A simple example of such a functional is

$$f(x, t, u, p) = x(\pi - x) f_1(x, t, u, p) + u\, f_2(x, t, u, p)$$

where f_1 and f_2 are two arbitrary continuous functionals.

Throughout the paper we shall denote by $k_1, k_2, \cdots$, various positive constants independent of all the variables involved and let

$$\begin{cases} 0 < m \leqslant \rho(x) & \leqslant M \\ |\rho'(x)| & \leqslant M \\ |\rho''(x)| & \leqslant M \end{cases} \tag{16}$$

3·1. *When* f *is Lipschitzian.*—Let us suppose that the function $f(x, t, \alpha, \beta)$ is defined for all real values of α and β, for all x in $(0\ \pi)$ and all $t \geqslant 0$ and is continuous with respect to all the variables. Further let f be

[6] The results of this article were read at the Fourth Annual Session of the Indian Academy of Sciences, held in December 1938, at Madras.

Lipschitzian with respect to α and β, that is to say

$$\{f(x,t,\alpha,\beta) - f(x,t,\alpha',\beta')\}^2 \leqslant k_1\{(\alpha-\alpha')^2 + (\beta-\beta')^2\}. \tag{17}$$

Now let

$$\begin{cases} f(x,t,u,p) \sim \sum_{n=1}^{\infty} \mathrm{F}_n\{t\,;u_1(t),\cdots\}\,\phi_n(x) \\ \mathrm{F}_n\{t\,;u_1(t),\cdots\} = \int_0^{\pi} f(x,t,u(x,t),p(x,t))\,\phi_n(x)\,dx. \end{cases} \tag{18}$$

If $v(x,t)$ is another function of the same form as (3) $v(x,t) \sim \Sigma v_n(t)\,\phi_n(x)$, $\frac{\partial v}{\partial x} = q(x,t)$, then by Reisz-Fischer theorem

$$\begin{aligned} &\sum_{n=1}^{\infty} \{\mathrm{F}_n(t\,;u_1(t),\cdots) - \mathrm{F}_n(t\,;v_1(t),\cdots)\}^2 \\ &\quad = \int_0^{\pi} \{f(x,t,u,p) - f(x,t,v,q)\}^2\,dx \\ &\quad \leqslant k_1\left\{\int_0^{\pi}(u-v)^2\,dx + \int_0^{\pi}(p-q)^2\,dx\right\} \\ &\quad \leqslant k_1\int_0^{\pi}(u-v)^2\,dx + \frac{k_1}{m}\int_0^{\pi}\rho\,(p-q)^2\,dx \\ &\quad = k_1\sum_{n:1}^{\infty}(u_n-v_n)^2 + \frac{k_1}{m}\sum_{n:1}^{\infty}\lambda_n(u_n-v_n)^2 \\ &\quad \leqslant \left(\frac{k_1}{\lambda_1}+\frac{k_1}{m}\right)\sum_{n:1}^{\infty}\lambda_n(u_n-v_n)^2 \\ &\quad = k_2\sum_{n:1}^{\infty}\lambda_n(u_n-v_n)^2. \end{aligned} \tag{19}$$

If (1) were to have a solution expressible in the form (3) we observe that on substituting the right side of (3) in (1) and equating the Fourier coefficients of both sides, $u_n(t)$ must satisfy the non-linear differential equation

$$\begin{aligned} &\frac{du_n}{dt} + \lambda_n u_n = -\mathrm{F}_n\{t\,;u_1(t),\cdots\} \\ &u_n(0) = c_n \qquad\qquad n:1,2,\cdots \end{aligned} \tag{20}$$

the solution of which is equivalent to that of the non-linear integral equations

$$u_n(t) = c_n e^{-\lambda_n t} - \int_0^t e^{-\lambda_n(t-s)}\,\mathrm{F}_n\{s\,;u_1(s),\cdots\}\,ds \qquad n:1,2,\cdots \tag{21}$$

If we put

$$v_n(t) = \sqrt{\lambda_n}\, u_n(t)\,; \quad \gamma_n = \sqrt{\lambda_n}\, c_n \tag{22}$$

and

$$\begin{aligned} \mathrm{F}_n\{s\,; u_1(s), \cdots\} &= \mathrm{F}_n\left(s\,; \frac{v_1(s)}{\sqrt{\lambda_1}}, \cdots\right) \\ &= \phi_n\{s\,; v_1(s), \cdots\} \end{aligned} \tag{23}$$

multiplying both sides of (21) by $\sqrt{\lambda_n}$ we have

$$v_n(t) = \gamma_n e^{-\lambda_n t} - \sqrt{\lambda_n} \int_0^t e^{-\lambda_n (t-s)}\, \phi_n\{s\,; v_1(s), \cdots\}\, ds \tag{24}$$

$$n : 1, 2, \cdots$$

The functionals ϕ_n satisfy the same conditions (19) and the kernels $\mathrm{K}_n(t, s) = \sqrt{\lambda_n}\, e^{-\lambda_n (t-s)}$ are such that

$$\begin{aligned} \int_0^t \mathrm{K}_n^2(t, s)\, ds &= \lambda_n \int_0^t e^{-2\lambda_n (t-s)}\, ds \\ &= \tfrac{1}{2}(1 - e^{-2\lambda_n t}) \\ &\leqslant \tfrac{1}{2}. \end{aligned} \tag{25}$$

If we suppose that the series

$$\sum_{n:1}^{\infty} \gamma_n^2 \tag{26}$$

is convergent, which implies that $u_0'(x)$ exists and is integrable L^2, we can solve the infinite system of non-linear integral equations (24) uniquely on account of (19), using the method of my earlier paper.[7] In fact if in (21) we put successively

$$\begin{cases} u_n^{0}(t) = 0 \\ u_n^{m}(t) = c_n e^{-\lambda_n t} - \displaystyle\int_0^t e^{-\lambda_n (t-s)}\, \mathrm{F}_n\{s\,; u_1^{m-1}(s), \cdots\}\, ds \end{cases} \tag{27}$$

$$m, n = 1, 2, \cdots$$

it can be shown that

$$\lim_{m \to \infty} v_n^{m}(t) = v_n(t) \tag{28}$$

exists for all n and all t in any finite interval (O T) and that

$$\lim_{m \to \infty} \sum_{n:1}^{\infty} (v_n^{m} - v_n)^2 = 0 \tag{29}$$

uniformly for all t in (O T).

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[7] See Foot-note 3.

Now from the convergence of the series $\Sigma\, \lambda_n u_n^2$ the absolute convergence of $\Sigma\, u_n$, and therefore of $\Sigma\, u_n \phi_n$ as ϕ_n are uniformly bounded, will follow because

$$\sum_{n:1}^{\infty} |u_n(t)| = \Sigma\, \sqrt{\lambda_n}\, |u_n| \cdot \frac{1}{\sqrt{\lambda_n}} \leqslant \left(\Sigma\, \lambda_n u_n^2 \cdot \Sigma\, \frac{1}{\lambda_n}\right)^{\frac{1}{2}}. \tag{30}$$

Again from (20) we observe that

$$\sum_{n:1}^{\infty} (u_n' + \lambda_n u_n)^2 \tag{31}$$

is uniformly convergent in (O T). We have thus proved the following :—

If the functional on the right of (1) *is defined for all values of* u *and* p *and is Lipschitzian with respect to them in addition to being uniformly continuous with respect to* x *and* t *and if the initially defined function* $u_0(x)$ *is such that* $u_0'(x)$ *is integrable* L^2, *we can solve* (1) *uniquely in the form* (3) *satisfying the boundary conditions* (2·1) *so that for all values of* t *in any finite interval* (O T) *the series* $\Sigma\, \lambda_n u_n^2$ *is uniformly convergent that is to say* p (x, t) *is integrable* L^2 *uniformly with respect to* t.

3·2. *When* f *has bounded partial derivatives.*—From (31) we cannot infer the convergence of the series $\Sigma\, \lambda_n^2 u_n^2$. If however we assume that $u_0''(x)$ is integrable L^2 that is $\Sigma\, \lambda_n^2 c_n^2$ is convergent and that $f(x, t, u, p)$ can be differentiated with respect to x, u and p whenever u and p are continuous, the partial derivatives f_x', f_u', f_p' being continuous and bounded, we can prove the convergence of the series $\Sigma\, \lambda_n^2 u_n^2$. For then we can prove that there exist constants k_3 and k_4 so that

$$\sum_{n:1}^{\infty} \lambda_n F_n^2 \{t; u_1(t), \cdots\} \leqslant k_3 + k_4 \sum_{n:1}^{\infty} \lambda_n^2 u_n^2 \tag{32}$$

Assuming (32) for the moment we multiply both sides of (27) by λ_n, square and add from $n = 1$ to ∞. Setting $w_n^m = \lambda_n u_n^m$ and $\delta_n = \lambda_n c_n$ and using Schwarz's inequality, (25) and (32) we get

$$\sum_{n:1}^{\infty} (w_n^m)^2 \leqslant 2 \sum_{n:1}^{\infty} \delta_n^2 + 2 \left\{\int_0^t e^{-\lambda_n (t-s)}\, F_n\, ds\right\}^2 \leqslant 2 k_5 + k_3 t + k_4 \int_0^t \sum_{n:1}^{\infty} (w_n^{m-1})^2\, ds. \tag{33}$$

$$m, n = 1, 2, \cdots$$

where we have put $\Sigma \delta_n^2 = \Sigma \lambda_n^2 c_n^2 = k_5$. From (33) we have by induction

$$(34) \qquad \sum_{n:1}^{\infty} (w_n^m)^2 \leqslant 2k_5\left(1 + k_4 t + \cdots + \frac{k_4^{m-1} t^{m-1}}{(m-1)!}\right) + k_3\left(t + \frac{k_4 t^2}{2!} + \cdots + \frac{k_4^{m-1} t^m}{m!}\right)$$

$$< 2k_5 e^{k_4 t} + \frac{k_3}{k_4}(e^{k_4 t} - 1)$$

$$= \left(2k_5 + \frac{k_3}{k_4}\right) e^{k_4 t} - \frac{k_3}{k_4}.$$

(34) shows that $\sum_{n:1}^{\infty} (w_n^m)^2$ is bounded uniformly for all values of m and all values of t in any finite interval (O T). Hence from (28) we infer the convergence of

$$(35) \qquad \sum_{n:1}^{\infty} w_n^2 = \sum_{n:1}^{\infty} \lambda_n^2 u_n^2$$

we shall now prove (32). We have

$$(36) \qquad \frac{df}{dx} = f_x' + f_u' \frac{\partial u}{\partial x} + f'_{\rho p} \frac{\partial (\rho p)}{\partial x}$$

and on account of the hypothesis on the partial derivatives of f we observe that k_6 and k_7 exist so that

$$(37) \qquad \rho\left(\frac{df}{dx}\right)^2 \leqslant k_6 + k_7\left[\rho p^2 + \left(\frac{\partial (\rho p)}{\partial x}\right)^2\right].$$

Now by (13) and (14)

$$(38) \qquad \begin{cases} \int_0^{\pi} \rho p^2 \, dx = \Sigma \lambda_n u_n^2 \\ \int_0^{\pi} \left(\frac{\partial (\rho p)}{\partial x}\right)^2 dx = \Sigma \lambda_n^2 u_n^2 \\ \int_0^{\pi} \rho\left(\frac{df}{dx}\right)^2 dx = \Sigma \lambda_n \mathrm{F}_n^2. \end{cases}$$

Integrating both sides of (37) with respect to x from 0 to π and using (38) we prove (32).

3·3 *When* f *is defined in a bounded domain.*—If the functional $f(x, t, u, p)$ in (1) is defined in the closed domain $0 \leqslant x \leqslant \pi$, $0 \leqslant t \leqslant \mathrm{T}$, $|u| \leqslant \mathrm{N}$ and $|p| \leqslant \mathrm{N}$ but otherwise satisfies the conditions of § 3·2 *viz.*, having continuous bounded partial derivatives (1) may be solved for

sufficiently small values of t. For

$$(39)\qquad \begin{cases} |u(x,t)| = |\Sigma u_n \phi_n| \leqslant \left(\Sigma \lambda_n^2 u_n^2 \cdot \Sigma \dfrac{\phi_n^2}{\lambda_n^2}\right)^{\frac{1}{2}} \\ |p(x,t)| = |\Sigma u_n \phi_n'| \leqslant \left(\Sigma \lambda_n^2 u_n^2 \Sigma \dfrac{\phi_n'^2}{\lambda_n^2}\right)^{\frac{1}{2}}. \end{cases}$$

If P is the maximum of $\left(\Sigma \dfrac{\phi_n^2}{\lambda_n^2}, \Sigma \dfrac{\phi_n'^2}{\lambda_n^2}\right)$ in $(0\,\pi)$ in order that $|u|, |p| \leqslant \mathrm{N}$ it is sufficient if

$$(40)\qquad \Sigma \lambda_n^2 u_n^2 \leqslant \frac{\mathrm{N}^2}{\mathrm{P}}.$$

From consideration of (34) it is obvious (40) can be effected if t is chosen so small that

$$(41)\qquad \left(2k_5 + \frac{k_3}{k_4}\right) e^{k_4 t} < \frac{\mathrm{N}^2}{\mathrm{P}} + \frac{k_3}{k_4}.$$

Now for $t \geqslant 0$, $e^{k_4 t} \geqslant 1$. Therefore a necessary condition for (41) is that

$$2k_5 + \frac{k_3}{k_4} < \frac{\mathrm{N}^2}{\mathrm{P}} + \frac{k_3}{k_4}.$$

or

$$(42)\qquad k_5 < \frac{\mathrm{N}^2}{2\,\mathrm{P}}.$$

(42) is a restriction on the initial condition as

$$k_5 = \sum_{n:1}^{\infty} \delta_n^2 = \sum_{n:1}^{\infty} \lambda_n^2 c_n^2 = \int_0^{\pi} \{(\rho u_0')'\}^2 \, dx$$

and we have the following :

If f (x, t, u, p) *is defined in the bounded four-dimensional domain* $0 \leqslant \mathrm{x} \leqslant \pi$, $0 \leqslant \mathrm{t} \leqslant \mathrm{T}$, $|\mathrm{u}| \leqslant \mathrm{N}$, $|p| \leqslant \mathrm{N}$ *and has bounded continuous partial derivatives with respect to* x, u *and* p *and* u_0'' (x) *is integrable* L^2, *the sum of the series* $\Sigma \lambda_n^2 c_n^2$ *being so small as to satisfy* (42) *we can solve* (1) *uniquely in the form* (3) *for sufficiently small values of* t, *such that* $\Sigma \lambda_n^2 u_n^2$ *is convergent.*

3·4. *When f has bounded partial derivatives of higher order.*—If we assume that f can be differentiated twice with respect to x, u and p, these derivatives being continuous and bounded and that $u_0'''(x)$ is integrable L^2, we can prove the convergence of $\Sigma \lambda_n^3 u_n^2$. We can then show as in (32) that there exist constants k_8 and k_9 so that

$$(43)\qquad \sum_{n:1}^{\infty} \lambda_n^2 \mathrm{F}_n^2 \leqslant k_8 + k_9 \Sigma \lambda_n^3 u_n^2$$

and we may argue as in § 3·3. From the convergence of $\Sigma \lambda_n^3 u_n^2$ absolute convergence of $\Sigma \lambda_n u_n$ will follow as in (30). More generally, if f has bounded

partial derivatives with respect to x, u and p of order r and if $u^{r+1}(x)$ is integrable L^2, we can prove the convergence of the series $\Sigma \lambda_n^{r+1} u_n^2$.

3·5. *Other boundary conditions.*—We may use the preceding discussion without great change to solve (1) for the boundary conditions (2·2), (2·3) and (2·4) as well. In the case (2·2) the preceding argument can be used without any change whatsoever, only we require the functional $f(x, t, u, p)$ to satisfy the boundary condition with regard to x. In the cases (2·3) and (2·4) since $\lambda_0 = 0$ is also an eigen-value of (5) there will be a slight change in the argument. We shall consider the boundary condition (2·3) as the case (2·4) can be similarly dealt with. If (1) were to have a solution in the form (3), then the summation will extend from $n = 0$ to ∞ and not 1 to ∞ as in the preceding discussion. In the place of (19) we will have

$$(19') \qquad \sum_{n=0}^{\infty} \{F_n[t; u_0(t), \cdots] - F_n[t; v_0(t), \cdots]\}^2 \leqslant k_{10}\{(u_0 - v_0)^2 + \sum_{n=1}^{\infty} \lambda_n (u_n - v_n)^2\}$$

On substituting (3) in (1) we have the equations

$$(20') \qquad \begin{cases} \dfrac{du_0(t)}{dt} = -F_0\{t; u_0(t), \cdots\} \\ \dfrac{du_n}{dt} + \lambda_n u_n = -F_n\{t; u_0(t) \cdots\} \\ u_n(0) = c_n; \quad n: 0, 1, 2, \cdots \end{cases}$$

which are equivalent to the infinite system of equations

$$(21') \qquad \begin{cases} u_0(t) = c_0 - \int_0^t F_0\{s; u_0(s), \cdots\} ds \\ u_n(t) = c_n e^{-\lambda_n t} - \int_0^t e^{-\lambda_n (t-s)} F_n\{s; u_0(s), \cdots\} ds \end{cases}$$

If we put

$$(22') \qquad \begin{cases} v_0(t) = u_0(t); v_n(t) = \sqrt{\lambda_n}\, u_n(t) & n: 1, 2, \cdots \\ \gamma_0 = c_0; \qquad \gamma_n = \sqrt{\lambda_n}\, c_n & n: 1, 2, \cdots \end{cases}$$

and multiply both sides of (21′) by $\sqrt{\lambda_n}$ we have

$$(24') \qquad v_n(t) = \gamma_n e^{-\lambda_n t} - \int_0^t K_n(t, s) F_n\{s; u_0(s), \cdots\} ds \qquad n: 0, 1, 2, \cdots$$

where $\quad K_0(t, s) = 1; K_n(t, s) = \sqrt{\lambda_n}\, e^{-\lambda_n (t-s)}$

we observe

$$\int_0^t \mathrm{K}_0^2\,(t, s)\,ds = t$$

$$\int_0^t \mathrm{K}_n^2\,(t, s)\,ds \leqslant \tfrac{1}{2} < t \quad \text{if } t > \tfrac{1}{2},\ n : 1, 2, \cdots$$

As in our discussions t is arbitrary we may assume $t \geqslant \frac{1}{2}$ so that in the place of (25) we have

$$\int_0^t \mathrm{K}_n^2\,(t, s)\,ds \leqslant t \qquad n : 0, 1, 2, \cdots \tag{25'}$$

These observations are sufficient to ensure that (24') can be solved uniquely by successive approximations. In fact with slight change in notation similar to the one shown in (22') we note that the discussions in § 3·1–3·4 can be used freely with the summation extending from $n = 0$ to ∞.

Systems of Equations

4. The above theory can be easily extended to any finite system of equations of the type (1). Consider for example the m-equations

$$\left\{\begin{array}{l} \dfrac{\partial}{\partial x}\left(\rho_1\,(x)\,\dfrac{\partial u_1}{\partial x}\right) - \dfrac{\partial u_1}{\partial t} = f_1\,(x, t\,;\, u_1, \cdots u_m\,;\, p_1, \cdots p_m) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \dfrac{\partial}{\partial x}\left(\rho_m\,(x)\,\dfrac{\partial u_m}{\partial x}\right) - \dfrac{\partial u_m}{\partial t} = f_m\,(x, t\,;\, u_1 \cdots u_m\,;\, p_1 \cdots p_m) \end{array}\right. \tag{44}$$

for the boundary conditions

$$u_i\,(0, t) = u_i\,(\pi, t) = 0\,;\ u_i\,(x, 0) \sim \sum_{n=1}^{\infty} c_n^i\,\phi_n^i\,(x) \qquad i : 1, 2, \cdots m \tag{45}$$

where $\phi_n^i\,(x)$ are the eigen-functions corresponding to the eigen-values λ_n^i of

$$\left\{\begin{array}{l} (\rho_i\,\phi')' + \lambda\,\phi = 0 \\ \phi\,(0) = \phi\,(\pi) = 0 \end{array}\right. \qquad i : 1, 2, \cdots m \tag{46}$$

Here the functions $\rho_i\,(x)$ have the same properties as the function $\rho\,(x)$ of (1).

If we set

$$u_i\,(x, t) \sim \Sigma\, u_n^i\,(t)\,\phi_n^i\,(x),\ u_n^i\,(0) = c_n^i \tag{47}$$

and

$$(48)\quad F_n^i\{t\,;\,u_1'(t),\cdots;u_1^i(t)\cdots\}=\int_0^{\pi} f_i(x,t,u_1\cdots;p_1\cdots)\,\phi_n^i(x)\,dx$$

$$i:1,2,\cdots m.$$

The equations (44) lead to the m-ply infinite system of equations

$$(49)\quad \frac{du_n^i(t)}{dt}+\lambda_n^i u_n^i=-F_n^i\{t\,;u_1'(t),\cdots;\cdots u_1^i(t),\cdots\}$$

or

$$(50)\quad u_n^i(t)=c_n^i e^{-\lambda_n^i t}-\int_0^t e^{-\lambda_n^i(t-s)}F_n^i\{s\,;u_1^1(s)\cdots\}\,ds$$

$$n:1,2,\cdots$$

$$i=1,2,\cdots m.$$

If the functionals f_i are defined for all real values of u_i and p_i and Lipschitzian with respect to them in addition to being continuous with respect to x and t we observe as in (19) that

$$(51)\quad \sum_{n:1}^{\infty}\{F_n^i(t\,;u_1',\cdots)-F_n^i(t\,;v_1'\cdots)\}^2$$

$$\leqslant k_{11}\{\sum_{i=1}^{m}\sum_{n=1}^{\infty}\lambda_n^i(u_n^i-v_n^i)^2\}.$$

Using (51) we can solve[8] the m-ply infinite system of integral equations (50) uniquely by successive approximations on assuming that $\Sigma\,\lambda_n^i\,c_n^{i2}$ are convergent for $i:1,2,\cdots m$. We can similarly extend the argument to the cases where the f_i's have bounded partial derivatives and obtain results similar to those in § 3. Systems of equations of the form (44) for other boundary conditions can be similarly studied.

Non-Linear Equations in three independent variables

5. The method we have developed permits itself to be applied easily to equations in more independent variables than two. As a simple extension we consider the equation in three independent variables, *viz.*,

$$(52)\quad \frac{\partial}{\partial x}\left(p(x,y)\frac{\partial u}{\partial x}\right)+\frac{\partial}{\partial y}\left(p(x,y)\frac{\partial u}{\partial y}\right)-\frac{\partial u}{\partial t}=f(x,y,t,u,u_x,u_y)$$

$$u_x=\frac{\partial u}{\partial x},\quad u_y=\frac{\partial u}{\partial y}$$

[8] See my paper "On an Infinite System of Non-Linear Integro-Differential Equations," *Proc. Ind. Acad. Sci.*, 1939, **9**, 410.

This paper will be an useful reference to the remarks in § 3·5.

where $p(x, y)$ is an essentially positive function, continuous and bounded together with its derivatives of the first two orders in and on the boundary of a closed domain D bounded by one or more regular curves C, in the x, y-plane. We shall first solve the equation (52) for the first boundary condition

$$(53) \qquad \begin{cases} u(x, y, t) = 0 \text{ on } c \text{ for all } t \geqslant 0. \\ u(x, y, 0) = u_0(x, y) \sim \sum_{n=1}^{\infty} c_n \omega_n(x, y) \end{cases}$$

where $\omega_n(x, y)$ are the eigen-functions of the equation

$$(54) \qquad \begin{cases} \frac{\partial}{\partial x}\left(p \frac{\partial \omega}{\partial x}\right) + \frac{\partial}{\partial y}\left(p \frac{\partial \omega}{\partial y}\right) + \mu\omega = 0 \\ \omega(x, y) = 0 \text{ on C} \end{cases}$$

the corresponding eigen-values being μ_n.

It is known[9] that $\sum_{n:1}^{\infty} \mu_n^{-2}$ is convergent and that if $\phi(x, y)$ is an arbitrary continuous function defined in D + C and vanishing on C we can develop $\phi(x, y)$ in a series of eigen-functions $\omega_n(x, y)$ so that

$$(55) \qquad \phi(x, y) \sim \sum_{n:1}^{\infty} a_n \omega_n(x, y); \quad a_n = \int_D \phi(x, y)\, \omega_n(x, y)\, dx\, dy$$

and

$$(56) \qquad \int_D \phi^2\, dx\, dy = \sum_{n=1}^{\infty} a_n^2.$$

Further if the first partial derivatives of $\phi(x, y)$ are continuous in D + C or at least integrable L^2, then

$$(57) \qquad \int_D p(\phi_x^2 + \phi_y^2)\, dx\, dy = \sum_{n=1}^{\infty} \mu_n a_n^2.$$

If we assume that the functional f vanishes on C for all $t \geqslant 0$ and that

$$(58) \qquad u(x, y, t) \sim \sum_{n:1}^{\infty} u_n(t)\, \omega_n(x, y)$$

$$(59) \qquad f(x, y, t, u, u_x, u_y) \sim \sum_{n:1}^{\infty} \mathrm{F}_n\{t, u_1(t), \cdots\}\, \omega_n(x, y)$$

we have, substituting (58) and (59) in (52) and equating the Fourier coefficients of both sides

$$(60) \qquad \begin{cases} \frac{du_n}{dt} + \mu_n u_n = -\mathrm{F}_n\{t; u_1(t), \cdots\} \\ u_n(0) = c_n \end{cases}$$

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[9] Lichtenstein, L., "Zur Analysis der unendlich vielen variablen," Zweite Abhandlung, *Math. Zeitschr.*, 1919, **3**, 127.

or

$$u_n(t) = c_n e^{-\mu_n t} - \int_0^t e^{-\mu_n (t-s)} F_n \{s ; u_1(s), \cdots\}\, ds \tag{61}$$

The equations (61) are exactly of the same form as (21) so that we can use the arguments of § 3 and prove similar results. Clearly it is enough if we only state the results as proofs are exactly along the same lines.

If the initially defined function $u_0(x, y)$ *is differentiable in* D, *the first partial derivatives being at least integrable in* D *so that* $\sum_{n=1}^{\infty} \mu_n c_n^2$ *is convergent, if the functional* $f(x, y, t, u, u_x, u_y)$ *is defined and continuous for all* x, y *in* $D + C$, $t \geqslant 0$ *and all real values of* u, u_x *and* u_y *and if it vanishes on* C *for all* $t \geqslant 0$ *and is Lipschitzian with respect to* u, u_x *and* u_y *we can solve* (52) *uniquely in the form* (58) *so that* $\Sigma \mu_n u_n^2$ *is uniformly convergent in any finite interval* (O T). *If on the other hand* f *has continuous and bounded partial derivatives with respect to* x, y, u, u_x *and* u_y *and if the second partial derivatives of* $u_0(x, y)$ *exist and are integrable* L^2, *so that* $\sum_{n=1}^{\infty} \mu_n^2 c_n^2$ *is convergent, then* $\Sigma \mu_n^2 u_n^2$ *will be convergent uniformly in* (O T). *If* f *is defined not for all values of* u, u_x *and* u_y *but in a bounded domain* $|u|, |u_x|, |u_y| \leqslant N$, *then the solution is possible only for sufficiently small values of* t.

5·1. We can similarly solve the equation (52) for the second boundary condition

$$\begin{cases} \dfrac{\partial u}{\partial n}(x, y, t) = 0 \text{ on C} \quad \text{for all } t \geqslant 0. \\ u(x, y, 0) = u_0(x, y) = \sum_{r=0}^{\infty} c_r \omega_r(x, y) \end{cases} \tag{62}$$

where $\omega_r(x, y)$ are the eigen-functions of

$$\begin{cases} \dfrac{\partial}{\partial x}\left(p \dfrac{\partial \omega}{\partial x}\right) + \dfrac{\partial}{\partial y}\left(p \dfrac{\partial \omega}{\partial y}\right) + \mu \omega = 0 \\ \dfrac{\partial \omega}{\partial n} = 0 \end{cases} \tag{63}$$

with the eigen-values μ_r, n denoting the interior normal at a point on C.

In view of the remarks made in § 4 a finite system of equations of the form (52) can also be solved uniquely by successive approximations.

I am thankful to Prof. M. R. Siddiqi for his kind help during my researches in this and allied topics.

ON NON-LINEAR PARTIAL DIFFERENTIAL EQUATIONS OF THE HYPERBOLIC TYPE

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§ 1. Consider the non-linear partial differential equation of the hyperbolic type in its normal form

$$\frac{\partial}{\partial x}\left(\rho\,(x)\,\frac{\partial u}{\partial x}\right) - \frac{\partial^2 u}{\partial t^2} = f\,(x, t, u, p, q) \qquad r = \frac{\partial u}{\partial x},\ q = \frac{\partial u}{\partial t} \tag{1}$$

for the boundary conditions

$$u\,(x, t) = 0 \text{ for } x = 0 \text{ and } x = \pi \tag{2}$$

$$u\,(x, 0) = u_0\,(x)\,;\ u_t\,(x, 0) = u_1\,(x), \tag{3}$$

where $\rho\ (x)$ is an essentially positive function continuous and bounded together with its first and second derivatives in $0 \leqslant x \leqslant \pi$. Applying the method of separation of variables we shall solve (1) in the form

$$u\,(x, t) \sim \sum_{n:1}^{\infty} u_n\,(t)\,\phi_n\,(x), \tag{4}$$

where $\phi_n\,(x)$ are the complete normal orthogonal eigen-functions of the Sturn-Liouville Differential system

$$\left.\begin{aligned} &\frac{d}{dx}\left(\rho\,\frac{d\phi}{dx}\right) + \lambda\,\phi = 0 \\ &\phi\,(0) = \phi\,(\pi) = 0 \end{aligned}\right\} \tag{5}$$

corresponding to the eigen-values λ_n. $u_0\ (x)$ and $u_1\ (x)$ can also be expanded in a series of Sturm-Liouville eigen-functions $\phi_n\ (x)$.

$$u_0\,(x) \sim \sum_{n:1}^{\infty} c_n\,\phi_n\,(x) \qquad c_n = u_n\,(0) \tag{6}$$

$$u_1\,(x) \sim \sum_{n:1}^{\infty} d_n\,\phi_n\,(x) \qquad d_n = u_n'\,(0) \tag{7}$$

The following equations, for the conditions (2) and (3)

$$\frac{\partial^2 u}{\partial x^2} - \frac{\partial^2 u}{\partial t^2} = u^2$$

$$\frac{\partial}{\partial x}\left\{\rho\,(x)\,\frac{\partial u}{\partial x}\right\} - \frac{\partial^2 u}{\partial t^2} = u^2$$

were studied by L. Lichtenstein[1] and M. R. Siddiqi[2] respectively and they showed that there exists one and only one solution in the form (4) for sufficiently small values of t. Their method can be applied easily to the case where we have on the right a functional $P(x, t, u) = \sum_{r:2}^{\infty} p_r(x, t)\, u^r$, but fails apparently if we have more general expressions as in (1). In the present paper we study the equation (1) adopting a slightly different procedure. In fact we make use of the idea of square convergence and not absolute convergence as was done by the authors quoted.

The results that we propose to prove can be stated in the following words. If the functional on the right of (1) can be expanded in a series of Sturm-Liouville eigen-functions $\phi_n(x)$ and if f is Lipschitzian with respect to u, p and q we can solve (1) uniquely in the form (4) such that $\sum_{n:1}^{\infty} \lambda_n u_n^2$ and $\sum_{n:1}^{\infty} (u_n')^2$ are uniformly convergent in any finite interval $(0\ T)$—that is p and q are integrable L^2 $(0 \leqslant x \leqslant \pi)$—whenever $u_0'(x)$ and $u_1(x)$ are integrable L^2. If, however, $u_0''(x)$ and $u_1'(x)$ are integrable L^2 and if the partial derivatives f_x', f_u', f_p', f_q' of f are bounded, then $\Sigma \lambda_n^2 u_n^2$ and $\Sigma \lambda_n (u_n')^2$ will also be convergent uniformly in $(O\ T)$. If f is defined in a bounded domain $|u|, |p|, |q| \leqslant N$, then the solution is possible for sufficiently small values of t.

The method of this paper permits itself to be applied to other boundary conditions, systems of equations, and equations in several variables.

§ 2. Throughout this paper we shall denote by $k_1, k_2, \cdots$, various positive constants independent of all the variables involved, and

$$(8) \qquad \begin{cases} 0 < m \leqslant \rho(x) & \leqslant M \\ |\rho'(x)| & \leqslant M \\ |\rho''(x)| & \leqslant M. \end{cases}$$

In addition to some of the familiar properties of Sturm-Liouville eigen-functions,[3] we assume the possibility of expanding $f(x, t, u, p, q)$ in a series of Sturm-Liouville eigen-functions $\phi_n(x)$. A necessary condition is that f satisfies the boundary conditions (2), that is

$$f(0, t, 0, p_0, 0) = f(\pi, t, 0, p_\pi, 0) = 0.$$

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[1] *Journal für Math.*, 1927, **158**, 80–91.

[2] *Proc. Camb. Phil. Soc.*, 1935, **31**, 195–202.

[3] I have given these properties in my paper "On Non-Linear Partial Differential Equations of Parabolic Type," *Proc. Ind. Acad. Sci.*, (A), 1939, **9**, 479.

So it is sufficient if f is continuous with respect to all the variables and

$$f(0, t, 0, \alpha, 0) = f(\pi, t, 0, \alpha, 0) = 0 \tag{9}$$

for all real α and all $t \geqslant 0$.

§ 2·1. *When f is Lipschitzian.*—Let us suppose that the function $f(x, t, \alpha, \beta, \gamma)$ is defined for all real values of α, β and γ, for all x in (O π) and all $t \geqslant 0$. Further let f be continuous with respect to x and t and Lipschitzian with respect to α, β and γ, so that

$$\{f(x, t, d, \beta, \gamma) - f(x, t, \alpha', \beta', \gamma')\}^2 \leqslant k_1 \{(\alpha - \alpha')^2 + (\beta - \beta')^2 + (\gamma - \gamma')^2\} \tag{10}$$

Now

$$\begin{cases} f(x, t, u, p, q) \sim \sum_{n:1}^{\infty} \mathrm{F}_n \{t ; u_1(t), \cdots ; u_1'(t), \cdots\} \phi_n(x) \\ \mathrm{F}_n \{t ; u_1(t), \cdots ; u_1'(t), \cdots\} = \int_0^{\pi} f(x, t, u, p, q) \phi_n(x)\, dx \end{cases} \tag{11}$$

and if $\bar{u}(x, t)$ is another function of the same form as (4)

$$\begin{aligned} &\sum_{n:1}^{\infty} \{\mathrm{F}_n(t ; u_1(t), \cdots ; u_1'(t), \cdots\} - \mathrm{F}_n(t ; \bar{u}_1(t), \cdots ; \bar{u}_1', (t), \cdots)\}^2 \\ &= \int_0^{\pi} \{f(x, t, u, p, q) - f(x, t, \bar{u}, \bar{p}, \bar{q})\}^2\, dx \\ &\leqslant k_1 \left\{ \int_0^{\pi} (u - \bar{u})^2\, dx + \int_0^{\pi} (p - \bar{p})^2\, dx + \int_0^{\pi} (q - \bar{q})^2\, dx \right\} \\ &\leqslant \left(\frac{k_1}{\lambda_1} + \frac{k_1}{m} \right) \Sigma \lambda_n (u_n - \bar{u}_n)^2 + k_1 \Sigma (u_n' - \bar{u}_n')^2 \\ &\leqslant k_2 \{\Sigma \lambda_n (u_n - \bar{u}_n)^2 + \Sigma (u_n' - \bar{u}_n')^2\}, \end{aligned} \tag{12}$$

where $k_2 = \max\left(k_1, \frac{k_1}{\lambda_1} + \frac{k_1}{m}\right)$ and $u_n' = \frac{du_n}{dt}$. If (1) were to have a solution expressible in the form (4) we observe that on substituting (4) in (1) and equating the Fourier coefficients of both sides, $u_n(t)$ must satisfy the non-linear differential equation

$$\begin{aligned} &\frac{d^2 u_n}{dt^2} + \lambda_n u_n = -\mathrm{F}_n(t) ; u_1(t), \cdots ; u_1'(t), \cdots) \\ &u_n(0) = c_n ; u_n'(0) = d_n ; n = 1, 2, \cdots \end{aligned} \tag{13}$$

The infinite system of differential equations (13) is equivalent to the system of non-linear integro-differential equations

$$\begin{aligned} u_n(t) = {} & c_n \cos \sqrt{\lambda_n}\, t + \frac{d_n}{\sqrt{\lambda_n}} \sin \sqrt{\lambda_n}\, t \\ & - \frac{1}{\sqrt{\lambda_n}} \int_0^t \sin \sqrt{\lambda_n}\, (t - s)\, \mathrm{F}_n(s ; u_1(s), \cdots ; u_1'(s), \cdots)\, ds. \end{aligned} \tag{14}$$

$n : 1, 2, \cdots$

Differentiating both sides of (14) with respect to t we observe that the integro-differential system (14) is in fact equivalent to the doubly infinite system of non-linear integral equations

$$(15)\quad \begin{cases} u_n(t) = c_n \cos \sqrt{\lambda_n}\, t + \dfrac{d_n}{\sqrt{\lambda_n}} \sin \sqrt{\lambda_n}\, t \\ \qquad - \dfrac{1}{\sqrt{\lambda_n}} \displaystyle\int_0^t \sin \sqrt{\lambda_n}\,(t-s)\, \mathrm{F}_n(s\,;\, u_1(s), \cdots ;\, u_1'(s), \cdots)\, ds \\ u_n'(t) = -\sqrt{\lambda_n}\, c_n \sin \sqrt{\lambda_n}\, t + d_n \cos \sqrt{\lambda_n}\, t \\ \qquad - \displaystyle\int_0^t \cos \sqrt{\lambda_n}\,(t-s)\, \mathrm{F}_n(s\,;\, u_1(s), \cdots ;\, u_1'(s), \cdots)\, ds \end{cases}$$

Thus the solution of (1) is equivalent to that of the system (15), which can be solved by successive approximations, following closely the method developed by the author in his paper[4] *"On an Infinite System of Integro-Differential Equations"*. Let us suppose that $u_0'(x)$ and $u_1(x)$ are integrable L^2 and write

$$(16)\quad \sum_{n:1}^{\infty} \lambda_n c_n^2 + \sum_{n:1}^{\infty} d_n^2 = k_3$$

$$(17)\quad \sum_{n:1}^{\infty} \mathrm{F}_n^2(t\,;\, 0, \cdots ;\, 0, \cdots) = \int_0^{\pi} f^2(x, t, 0, 0, 0)\, dx < k_4$$

and

$$(18)\quad \begin{cases} u_n^0(t) = 0 \\ u_n^m(t) = c_n \cos \sqrt{\lambda_n}\, t + \dfrac{d_n}{\sqrt{\lambda_n}} \sin \sqrt{\lambda_n}\, t \\ \qquad - \dfrac{1}{\sqrt{\lambda_n}} \displaystyle\int_0^t \sin \sqrt{\lambda_n}\,(t-s)\, \mathrm{F}_n\{s\,;\, u_1^{m-1}(s), \cdots ;\, u_1'^{m-1}(s), \cdots\}\, ds \\ u_n'^0(t) = 0 \\ u_n'^m(t) = -\sqrt{\lambda_n}\, c_n \sin \sqrt{\lambda_n}\, t + d_n \cos \sqrt{\lambda_n}\, t \\ \qquad - \displaystyle\int_0^t \cos \sqrt{\lambda_n}\,(t-s)\, \mathrm{F}_n\{s\,;\, u_1^{m-1}(s), \cdots ;\, u_1'^{m-1}(s), \cdots\}\, ds. \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad n : 1, 2, \cdots ;\ m : 1, 2, \cdots \end{cases}$$

Then, if we set,

$$(19)\quad \begin{cases} y_n^m(t) = \sqrt{\lambda_n}\, u_n^m(t) \\ z_n^m(t) = u'^m_n(t) \end{cases}$$

[4] *Proc. Ind. Acad. Sci.*, (A), 1939, **9**, 410–418.

we can show using (12), (16) and (17) that

$$\text{(20)} \qquad \operatorname*{Lim}_{m \to \infty} y_n^m(t) = y_n(t)\,; \quad \operatorname*{Lim}_{m \to \infty} z_n^m(t) = z_n(t)$$

exist for every n uniformly in any finite interval (O T) and, further

$$\text{(21)} \qquad \operatorname*{Lim}_{m \to \infty} \sum_{n:1}^{\infty} (y_n^m - y_n)^2 = \operatorname*{Lim}_{m \to \infty} \sum_{n:1}^{\infty} (z_n^m - z_n)^2 = 0$$

uniformly in (O T). The functions $u_n(t) = \dfrac{y_n(t)}{\sqrt{\lambda_n}}$ and $u_n'(t) = z_n(t)$ so obtained are in fact unique solutions of (15). The convergence of the series $\sum_{n:1}^{\infty} y_n^2 = \sum_{n:1}^{\infty} \lambda_n u_n^2$ and $\sum_{n:1}^{\infty} (u_n')^2$, which follows from (21) implies that $\dfrac{\partial u}{\partial x}$ and $\dfrac{\partial u}{\partial t}$ exist and are integrable $L^2(0, \pi)$. Thus we have

THEOREM 1. *If* $u_0'(x)$ *and* $u_1(x)$ *are integrable* $L^2(0\pi)$ *and if* $f(x, t, u, p, q)$ *is defined for all real values of* u, p *and* q *and is Lipschitzian with respect to them in addition to being continuous with respect to* x *and* t; *then we can solve* (1) *uniquely in the form* (4) *such that* $\Sigma \lambda_n u_n^2(t)$ *and* $\Sigma [u_n'(t)]^2$ *are uniformly convergent that is to say* p (x, t) and q (x, t) *are integrable* L^2 *uniformly in* t.

§ 2·2. *When* f *has bounded partial derivatives.*—From the known properties of Sturm-Liouville eigen-functions $\phi_n(x)$ and the eigen-values λ_n, the absolute convergence of $\sum_{n:1}^{\infty} u_n(t)\,\phi_n(x)$ will follow, as

$$\text{(22)} \qquad \sum_{n:1}^{\infty} |u_n \phi_n| \leqslant \left\{ \Sigma \lambda_n u_n^2 \; \Sigma \frac{\phi_n^2}{\lambda_n} \right\}^{\frac{1}{2}}.$$

But we cannot prove the convergence of the series $\sum_{n:1}^{\infty} \lambda_n^2 u_n^2$ and $\sum_{n:1}^{\infty} \lambda_n (u_n')^2$ from the above discussion. We have to assume more about the initial functions and also $f(x, t, u, p, q)$. Let us suppose that $u_0''(x)$ and $u_1'(x)$ exist and are integrable L^2 and that f can be differentiated with respect to x whenever u, p and q are continuous and that f_x, f_u, f_p, f_q are bounded uniformly. Then it can be shown that

$$\text{(23)} \qquad \sum_{n:1}^{\infty} \lambda_n F_n^2 \leqslant k_5 + k_6 \sum_{n:1}^{\infty} \{\lambda_n^2 u_n^2 + \lambda_n (u_n')^2\}$$

If we write

$$\text{(24)} \qquad \sum_{n:1}^{\infty} \lambda_n^2 c_n^2 + \sum_{n:1}^{\infty} \lambda_n d_n^2 = k_7$$

we have from (18) and (23)

$$(25)\quad \begin{cases} \sum_{n:1}^{\infty} \lambda_n^2 (u_n^m)^2 \leqslant 3k_7 + 3t \int_0^t [k_5 + k_6 \sum_{n:1}^{\infty} \{\lambda_n u_n^{m-1})^2 + \lambda_n (u_n'^{m-1})^2\}] ds \\ \sum_{n:1}^{\infty} \lambda_n (u_n'^m)^2 \leqslant 3k_7 + 3t \int_0^t [k_5 + k_6 \sum_{n:1}^{\infty} \{(\lambda_n u_n^{m-1})^2 + \lambda_n (u_n'^{m-1})^2\}] ds. \end{cases}$$

Adding, we have

$$(26)\quad \sum_{n=1}^{\infty} \{(\lambda_n u_n^m)^2 + \lambda_n (u_n'^m)^2\} \leqslant 6k_7 + 6k_5 t^2 + 6k_6 t \int_0^t \sum_{n:1}^{\infty} \{(\lambda_n u_n^{m-1})^2 + \lambda_n (u_n'^{m-1})^2\} ds$$

$$< 6k_7 \left(1 + 6k_6 t^2 + \cdots + \frac{(6k_6 t^2)^{m-1}}{(m-1)!}\right) + \frac{k_5}{k_6}\left(6k_6 t^2 + \cdots + \frac{(6k_6 t^2)^m}{m!}\right) \text{ by induction}$$

$$< 6k_7 e^{6k_6 t^2} + \frac{k_5}{k_6}(e^{6k_6 t^2} - 1)$$

$$= \left(6k_7 + \frac{k_5}{k_6}\right) e^{6k_6 t^2} - \frac{k_5}{k_6}.$$

(26) shows that $\sum_{n:1}^{\infty} (\lambda_n u_n^m)^2$ and $\sum_{n:1}^{\infty} \lambda_n (u_n'^m)^2$ are uniformly bounded for all m and all t in (O T), so that from (20) we observe the convergence of $\Sigma \lambda_n^2 u_n^2$ and $\Sigma \lambda_n (u_n')^2$. To prove (23) we observe that

$$\frac{df}{dx} = f_x' + f_u' p + f_\rho \rho' \frac{\partial \rho p}{\partial x} + f_q' \frac{\partial q}{\partial x}$$

so that

$$\rho \left(\frac{df}{dx}\right)^2 \leqslant k_8 + k_9 \left\{\rho p^2 + \left(\frac{\partial \rho p}{\partial x}\right)^2 + \rho \left(\frac{\partial q}{\partial x}\right)^2\right\}.$$

Integrating both sides with respect to x from 0 to π we prove (23).

§ 2·3. *When* f *is defined in a bounded domain.*—Now using (26) in (25) we have

$$(27)\quad \left.\begin{matrix} \sum_{n:1}^{\infty} (\lambda_n u_n^m)^2 \\ \sum_{n:1}^{\infty} \lambda_n (u_n'^m)^2 \end{matrix}\right\} \leqslant 3k_7 \left(1 + 6\lambda_6 t^2 + \cdots + \frac{(6k_6 t^2)^{m-1}}{(m-1)!}\right) + \frac{k_5}{2k_6}\left(6x_6 t^2 + \cdots + \frac{(6k_6 t^2)^m}{m!}\right)$$

$$< \left(3k_7 + \frac{k_5}{2k_6}\right) e^{6k_6 t^2} - \frac{k_5}{2k_6}$$

Let us suppose that the functional $f(x, t, u, p, q)$ is defined for $|u|, |p|, |q| \leqslant N$ where N is a positive number but otherwise satisfies the previous conditions, *viz.*, having bounded partial derivatives. We can now prove the existence of a solution for sufficiently small values of t. For

$$(28)\qquad \left\{\begin{aligned} |u(x,t)| &= |\Sigma u_n \phi_n| \leqslant \left\{\Sigma \lambda_n^2 u_n^2 \Sigma \frac{\phi_n^2}{\lambda_n^2}\right\}^{\frac{1}{2}} \\ |p(x,t)| &= |\Sigma u_n \phi_n'| \leqslant \left\{\Sigma \lambda_n^2 u_n^2 \Sigma \left(\frac{\phi_n'}{\lambda_n}\right)^2\right\}^{\frac{1}{2}} \\ |q(x,t)| &= |\Sigma u_n' \phi_n| \leqslant \left(\Sigma \lambda_n (u_n')^2 \Sigma \frac{\phi_n^2}{\lambda_n}\right)^{\frac{1}{2}}. \end{aligned}\right.$$

If P is the maximum of $\Sigma \frac{\phi_n^2}{\lambda_n^2}, \Sigma \frac{\phi_n^2}{\lambda_n}, \Sigma \left(\frac{\phi_n'}{\lambda_n}\right)^2$ in $0 \leqslant x \leqslant \pi$, clearly in view of (28), in order that $|u|, |p|, |q| \leqslant N$, it is sufficient if

$$(29)\qquad \begin{aligned} \Sigma \lambda_n^2 u_n^2 &\leqslant \frac{N^2}{P} \\ \Sigma \lambda_n (u_n')^2 &\leqslant \frac{N^2}{P} \end{aligned}$$

From consideration of (27), it is obvious that (29) will be realised if

$$(30)\qquad \left(3k_7 + \frac{k_5}{k_6}\right) e^{6k_6 t^2} < \frac{N^2}{P} + \frac{k_5}{2k_6}$$

we can choose t so small as to satisfy (30), only if

$$3k_7 + \frac{k_5}{k_7} < \frac{N^2}{P} + \frac{k_5}{2k_6}$$

or

$$(31)\qquad k_7 < \frac{N^2}{3P}.$$

In view of (24), (31) is a restriction on the initial function.

We have thus

THEOREM 2. *If* $f(x, t, u, p, q)$ *is defined in the bounded five-dimensional domain* $0 \leqslant x \leqslant \pi$; $0 \leqslant t \leqslant T$; $|u|, |p|, |q| \leqslant N$ *and has bounded continuous partial derivatives* f_x, f_u, f_p, f_q, *and* $u_0''(x)$ *and* $u_1'(x)$ *exist and are integrable* L^2, *the sum defined in* (24) *satisfying the inequality* (31), *we can solve* (1) *uniquely in the form* (4) *so that for sufficiently small values of* t, $\Sigma \lambda_n^2 u_n^2$ *and* $\Sigma \lambda_n (u_n')^2$ *are convergent, that is* $\frac{\partial^2 u}{\partial x}$ *and* $\frac{\partial^2 u}{\partial x \partial t}$ *—and therefore from* (1) *also* $\frac{\partial^2 u}{\partial t^2}$ *—are integrable* L^2.

§ 3. From the convergence of $\Sigma \lambda_n^2 u_n^2$ and $\Sigma \lambda_n (u_n')^2$ we can prove as in (22) the absolute convergence of $\Sigma u_n \phi_n'$ and $\Sigma u_n' \phi_n$. In as far as the non-linear partial differential equation (1) is equivalent to a doubly infinite system of non-linear integral equations, which can be solved by successive approximations even as in the case of a singly infinite system of equations, all the remarks that we made[5] with regard to non-linear partial differential equations of the parabolic type hold good in the case of hyperbolic type of equations as well.

Thus (*a*) If f has bounded partial derivatives with respect to x, u, p, and q of order r we can show that $\Sigma \lambda_n^{r+1} u_n^2$ and $\Sigma \lambda_n^r (u_n')^2$ are convergent.

(*b*) If instead of the boundary conditions (2) we have one of the following :

$$(2\cdot1) \qquad u(0, t) = \frac{\partial u}{\partial x}(\pi, t) = 0$$

$$(2\cdot2) \qquad \frac{\partial u}{\partial x}(0, t) = \frac{\partial u}{\partial x}(\pi, t) = 0$$

$$(2\cdot3) \qquad u(0, t) = u(\pi, t) \; ; \; \rho(0) \frac{\partial u}{\partial x}(0, t) = \rho(\pi) \frac{\partial u}{\partial x}(\pi, t).$$

We can still reduce the equation (1) to a doubly infinite system of integral equations which can be solved uniquely by successive approximations.

(*c*) The method of our paper can be extended easily to finite system of equations of the form (1), *viz.*,

$$\frac{\partial}{\partial x}\left(\rho_i(x) \frac{\partial u_i}{\partial x}\right) - \frac{\partial^2 u_i}{\partial t^2} = f_i(x, t, u_1, u_2, \cdots p_1, p_2, \cdots q_1, q_2, \cdots)$$

$$i = 1, 2, \cdots \mu$$

where u's satisfy one or other of the boundary conditions (2) to (2·3) and the initial conditions

$$u_i(x, 0) = g_i(x) \; ; \; \frac{\partial u_i}{\partial t}(x, 0) = h_i(x) \qquad i : 1, 2, \cdots \mu$$

We are led to 2μ-ply infinite system of integral equations which can also be solved by successive approximations, when f_i, g_i and h_i satisfy the conditions of Theorem 1 or Theorem 2.

(*d*) The solutions of equations of this type with more independent variables than two are equally simple. Thus, the equation

$$\frac{\partial}{\partial x}\left\{p(x, y) \frac{\partial u}{\partial x}\right\} + \frac{\partial}{\partial y}\left\{p(x, y) \frac{\partial u}{\partial y}\right\} - \frac{\partial^2 u}{\partial t^2} = f(x, t, u, u_x, u_y u_t)$$

[5] See the paper cited in Foot-note 3.

for the first or second boundary condition

$$u(x, y, t) = 0 \text{ on } c \text{ for all } t \geqslant 0$$

$$\frac{\partial u}{\partial n}(x, y, t) = 0 \text{ on } c \text{ for all } t \geqslant 0$$

where c is a regular closed curve bounding a domain D in the x, y-plane, and n is the interior normal on c; and for the initial conditions

$$u(x, y, 0) = u_0(x, y) \sim \Sigma c_n \omega_n(x, y)$$

$$u_t(x, y, 0) = u_1(x, y) \sim \Sigma d_n \omega_n(x, y)$$

can be solved by the method of the previous sections. In fact a solution in the form

$$u(x, y, t) \sim \Sigma u_n(t) \omega_n(x, y),$$

$u_n(t)$ satisfying the same integro-differential equation as (14), can be found, where $\omega_n(x, y)$ are the eigen-functions

$$\frac{\partial}{\partial x}\left\{p(x, y)\frac{\partial \omega}{\partial x}\right\} + \frac{\partial}{\partial y}\left\{p(x, y)\frac{\partial \omega}{\partial y}\right\} + \mu\omega = 0$$

for the corresponding boundary conditions

$$\omega(x, y) = 0 \text{ on } c \text{ or } \frac{\partial \omega}{\partial n}(x, y) = 0 \text{ on } c.$$

Indeed Theorems 1 and 2 have their complete analogues in this case as well.

A SIMPLE CYLINDRICAL LENS SPECTROGRAPH FOR THE OPTICAL DETERMINATION OF THE CONCENTRATION OF OZONE IN THE ATMOSPHERIC LAYERS NEAR THE GROUND

By M. W. Chiplonkar, M.Sc.

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(Communicated by Dr. K. R. Ramanathan, D.Sc.)

The optical absorption of ozone in the region 3150 to 2200 Å has been used by a number of workers for the determination of the amount of ozone in the atmosphere, since the pioneer use of it for this purpose by Fabry and Buisson[1] in 1920. Buisson, Jousseran and Rouard in France,[2] Götz and Ladenburg,[3] and Götz and Maier–Leibnitz[4] in Switzerland have determined the relative attenuations of ultra-violet light of different wave-lengths by exposing similar spectrographs at different distances from a source of radiation and calculated from the results that the amount of ozone normally present in the air-layers near the ground is in the neighbourhood of 2×10^{-3} cm. at N.T.P. per kilometre length of air. The present note describes a simple prism spectrograph for the photometric determination of the amount of ozone in the air-layers near the ground and the preliminary results of some measurements made with it at Poona.

Description of the Spectrograph

The usual methods of photographing the spectrum of a distant source of light of small angular extent are to throw an image of the source on the slit of the spectrograph by means of a cylindrical lens so that the point-image is elongated into a line, or to move the photographic plate in a direction perpendicular to the length of the spectrum. For some purposes, an objective prism spectrograph in which the slit and collimator are dispensed with, offers advantages but the point-images obtained with it are not convenient for photometric purposes. If the spherical camera lens of the objective prism spectrograph is replaced by a cylindrical lens with its axis parallel to the refracting edge of the prism, a spectrum with the usual appearance can be obtained, and if an optical wedge is added near the photographic plate with the slope of the wedge parallel to the length of the spectral lines the comparative intensities of the lines in the spectrum can be easily determined.

A spectrograph constructed on this principle is shown in Figs. 1 and 2. In Fig. 1, T is a cylindrical tube for directing the instrument towards the

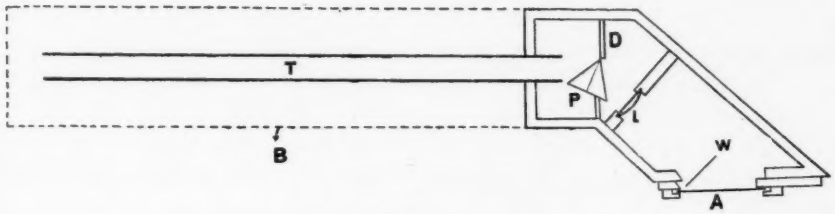

FIG. 1

Cylindrical objective prism quartz spectrograph

T = Metal Tube	L = Cylindrical quartz lens
B = Wooden base	W = Optical Wedge (quartz)
P = Cornu Prism	A = Photographic plate

source and preventing light from other undesired sources from falling on the prism, P is a Cornu prism of quartz, L a cylindrical lens, W an optical wedge and A the photographic plate. In Fig. 2, a sighting tube is shown parallel to the tube T which helps to direct the instrument in the proper direction.

The instrument was used to determine the ozone near ground level at Poona on a few days in the clear season of 1937. A quartz mercury arc lamp was used as the source of light and was placed on the roof of the Fergusson College Physical Laboratory. The current through the arc was kept constant with the help of a rheostat and ammeter and a fan was used to drive away any accumulation of ozone in the neighbourhood of the arc. The spectrum of the arc was photographed from three different places : (1) From the Fergusson College Hospital, distant 0·3 km. from the arc ; (2) From the tower of the Meteorological Office, distant 1·6 km. ; (3) From the Parnakuti hill, distant 4·8 km. The times of exposure varied from a few seconds at the first distance to 5 hrs. at the last. The observations were usually made on nights when the evening sea-breeze had cleared the haze over the city and its environs.

The nature of the photographs obtained without the wedge will be seen from Fig. 3 (*a*) in which are shown the spectra of a quartz mercury arc at distances of 0·3, 1·6 and 4·8 km. respectively. The appearance of the spectra when the quartz wedge is in position is shown in Fig. 3 (*b*).

The method of calculating the amount of ozone is briefly outlined below :

Let I_1 be the intensity of light of wave-length λ_1 received at a distance r from the source. Then

$$I_1 = \frac{L_{\lambda_1}}{4\pi r^2} 10^{-(a_1 x + \beta_1 + \gamma_1) r} \quad (1)$$

when L, is the power radiated by the source in light of wave-length λ_1,

x is the amount of ozone in the atmosphere per unit length of path,

a_1 is the decimal absorption coefficient of ozone,

β_1 the attenuation of light per unit length of path due to molecular scattering and γ_1 the attenuation coefficient due to dust or other suspended particles.

Similarly, the intensity I_2 of the light of wave-length λ_2 is given by

$$I_2 = \frac{L_{\lambda_2}}{4\pi r^2} 10^{-(a_2 x + \beta_2 + \gamma_2) r} \quad (2)$$

From (1) and (2)

$$\frac{I_1}{I_2} = \frac{L_1}{L_2} 10^{-(a_1 - a_2) xr - (\beta_1 - \beta_2) r - (\gamma_1 - \gamma_2) r}. \quad (3)$$

Similarly for another distance r'

$$\frac{I_1'}{I_2'} = \frac{L_1}{L_2} 10^{-(a_1 - a_2) xr' - (\beta_1 - \beta_2) r' - (\gamma_1 - \gamma_2) r'} \quad (4)$$

From (3) and (4)

$$x = \frac{(\log I_2 - \log I_2') - (\log I_1 - \log I_1') + (\beta_2 - \beta_1)(r - r') + (\gamma_2 - \gamma_1)(r - r')}{(a_1 - a_2)(r - r')} \quad (5)$$

If the wedge constants for the wave-lengths λ_1 and λ_2 are known, the ratios I_1/I_1' and I_2/I_1' can be calculated easily from the lengths of the lines in the wedge spectrum, β_1 and β_2 can be determined from Rayleigh's scattering formula with the correction for the depolarisation of the scattered light; and the difference $\lambda_2 - \lambda_1$ is negligible compared with $(a_2 - a_1) x$ and $(\beta_2 - \beta_1)$, particularly if λ_1 and λ_2 are near each other and one of them is outside the region of ozone absorption and the other within it, and the atmosphere does not contain large chemical impurities. In Poona, on days when the evening sea-breeze sets in, the atmosphere is generally free from dust and haze for a few hours after sunset.

For the preliminary measurements at Poona, the quartz wedge of the Dobson spectrograph was used. This has a wedge-constant of about 1·38 per centimetre in the ultra-violet region near 3000 Å. The amounts of ozone obtained at Poona varied from 1 to 5×10^{-3} cm. ozone at N.T.P. per kilometre of path which is of the same order of quantities as those obtained in

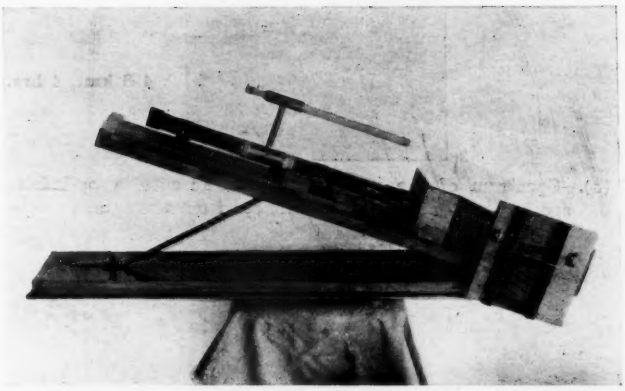

FIG. 2.—Photograph of the cylindrical lens spectrograph

FIG. 3 (*a*).—Spectrum of the mercury arc taken with a cylindrical lens spectrograph at different distances from the source

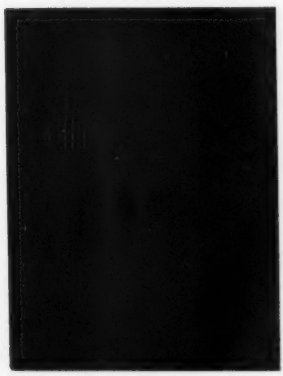

FIG. 3 (*b*).—Spectrum of a quartz mercury arc taken with a cylindrical lens spectrograph and an optical wedge

France and Switzerland. For an accurate determination of the daily variations in the amount of ozone a wedge with a smaller constant should be used. Arrangements are being made to obtain a suitable wedge and extend the observations.

The work was started at the suggestion of Dr. K. R. Ramanathan and I am thankful to him for his interest in the work. My thanks are also due to the Director-General of Observatories, Poona, and to Professor Joshi of the Fergusson College, Poona, for the facilities they gave me. The quartz cylindrical lens was purchased out of a grant from the University of Bombay.

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THE CONDENSATION OF ALDEHYDES

Part III. Of *p*-Tolylaldehyde with Amides

Part XI. Of *p*-Tolylaldehyde with Malonic Acid and Malonanilic Acid

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p-Tolylaldehyde when heated with one of the amides described below combines to give compounds of the type of *p*-tolylidene-bisamides, very like the benzylidenebisamides obtained from benzaldehyde by Bülow and others.[1] It is found that acetamide, propionamide, benzamide and phenylacetamide undergo this condensation merely by heating the two alone, the presence of pyridine not having any appreciable influence on the yields. Formamide, however, remained unaffected even after prolonged heating, but the condensation was effected in the presence of a trace of pyridine. The yields were not high, being below 50% of theory. All the condensation-products were saturated, and did not affect Baeyer's reagent.

Experimental

Condensation with Formamide.—*p*-Tolylaldehyde 3 g., formamide 2·2 g. and pyridine (0·3 c.c.) (1 : 2 : 0·15 mol.) were heated together at 175–80° for three hours. Longer or higher heating gave a dark brown colour, and lower temperatures were ineffective. The flask was taken out of the oils bath when the colour showed signs of darkening. On cooling, pale yellow crystals separated, which were filtered out and washed well with water and boiling alcohol or boiling acetone, respectively. The crystals were insoluble in the usual solvents. Repeated washing as above gave a sample melting at 287° C.

Nitrogen found : 14·54%; *p*-tolylidene-bisformamide $C_{10}H_{12}O_2N_2$ require 14·59%.

The product weighed 0·7 g. and the yield was 14·6% of theory.

Condensation with Acetamide.—3 g. Aldehyde and 3 g. acetamide (1 : 2 mol.) were heated for 4 hours at 120–125°. The whole became a homogeneous mass at about 105° and gave out water vapours. After 1·5 hours' heating, a solid began to separate, which increased in amount after the heating was stopped and the flask was cooled. The unaffected aldehyde was removed

by extraction with ether, and the solid was crushed with cold water to remove the acetamide. The crude product on recrystallisation from hot dilute alcohol came out in milk-white silky needles, melting at 274° C. It weighed 1·5 g. and the yield was 27·3% of theory.

Nitrogen found : 12·90% ; *p*-tolylidene-bisacetamide $C_{12}H_{16}O_2N_2$ requires 12·73%.

Condensation with Propionamide.—The aldehyde 3 g. and the amide 3·6 g. (1 : 2 mol.) were heated at 120° for 4 hours ; the mixture behaved as in the acetamide condensation, and the product was taken out in the same way, being recrystallised from hot alcohol or hot acetone. Milk-white silky needles melted at 232° C. Yield = 1·5 g. or 24·2%.

Nitrogen found : 11·35% ; the *p*-tolylidene-bispropionamide $C_{14}H_{20}O_2N_2$ requires 11·29%.

Condensation with Benzamide.—The aldehyde 3 g. and the amide 6 g. (1 : 2 mol.) were heated together at 120–125° for 3 hours. Within half-an-hour a crystalline white solid began to make its appearance. It was taken out in the same way and the same was purified as before. Milk-white needles, m.p. 230° C. Weighed 3·5 g. or 40·7% of theory.

Nitrogen found : 8·67% ; the bisbenzamide $C_{22}H_2O_2N_2$ requires 8·14%.

Condensation with Phenylacetamide.—1·5 g. of the aldehyde and 3·4 g. of the amide (1 : 2 mol.) were heated for 3 hours at 125–130°. The mixture fused to a homogeneous mass and gave out water vapours at 120°, and solid particles began to come out after 1·5 hours. The product was taken out and purified as before, but was found to be very little soluble in cold alcohol or acetone. Recrystallized from the hot solvent it came out as white silky needles, m.p. 238° C. Weight 2 g. = yield 43% of theory.

Nitrogen found : 7·93% ; the bisphenylacetamide $C_{24}H_{24}O_2N_2$ requires 7·53%.

* * *

Condensation with Malonic Acid and Malonanilic Acid

In our paper on the condensation of aromatic aldehydes with malonanilic acid, it was stated that this acid condenses with *p*-tolylaldehyde giving about 71% yield of the cinnamanilide. The work, however, was not described further as sufficient amount of the aldehyde or of the condensation-product was not in hand for analytical purposes.[2] This work is now concluded and confirmed, the details are given below. The condensation was brought about by a trace of pyridine and the product did not contain any acid.

The condensation with malonic acid was carried out as usual, the yield of the *p*-methylcinnamic acid being quantitative when a trace of pyridine was used and only slightly less in the absence of any condensing agent.

Condensation was found to take place similarly with ethyl malonate.

Condensation with Malonanilic Acid.—1·2 g. *p*-Tolylaldehyde, 1·8 g. malonanilic acid and a trace of pyridine (1 : 1 : 0·15 mol.) were heated on a water-bath for 5 hours. In the course of an hour, fusion to a homogeneous mass took place and gas was liberated. After 5 hours' heating, it was left overnight, when most of it had solidified leaving a little of the unused liquid aldehyde. This was removed by means of ether, and the solid treated as usual with sodium bicarbonate solution. The bicarbonate extract did not give any acid product on acidification. The anilide which did not dissolve was purified by crystallisation from hot dilute alcohol. It came out in tiny white shining needles, melted at 184° C. and weighed 1·7 g. (yield 71·7%).

Nitrogen found : 5·86%; the *p*-methylcinnamanilide $C_{16}H_{15}ON$ requires N = 5·93%.

Condensation with Malonic Acid.—The aldehyde, malonic acid and pyridine were taken as 1 : 1 : 0·15 mol. and heated on the water-bath for 5 hours. The methylcinnamic acid was taken out in the usual way. The yield was about 93%: with acid malonic in 1·5 mol. proportion, the yield was about 99%. When no pryidine was used, the yield came up to about 91%, but the product was less pure and the heating was for 5·5 hours.

It melted at 197–198° C. (It has been prepared before by Perkin's reaction by several workers.[3])

Summary

The condensation of *p*-tolylaldehyde with five different amides, and with malonic acid and malonanilic acid have been described. The amides give bisamide products, and malonanilic acid the cinnamamilide. The yield with malonic acid is almost quantitative.

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CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XII. The Influence of Groups and of other Factors

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The reduced yields of the hydroxy-cinnamic acids obtained from the condensations of malonic acid with hydroxy-benzaldehydes have been generally recognised as due to the steric hindrance caused by the hydroxyl group present on the nucleus. This is most evident in the case of salicylaldehyde where the hydroxy group is *ortho* to the aldehyde group. That this inhibitive effect is appreciably, and sometimes largely, modified, when the hydroxy group is replaced by the methoxy group has also been pointed out in an earlier paper.[1] In the same paper was also pointed out the increase in the inhibitive influence in the case of 2 : 4-resorcylaldehyde, wherein the nucleus contained two hydroxy groups, one of which was *ortho* to the aldehyde. The highest yield obtained here was only 46%, in contrast with 64% obtained in the case of the mono-hydroxy aldehyde, salicylaldehyde.

These observations are further corroborated in the present paper wherein the condensations of protocatechuicaldehyde, vanillin and veratraldehyde under comparable conditions have been investigated. The three may be looked upon as belonging to a series, with two hydroxy groups in protocatechuicaldehyde, one hydroxy and one methoxy group in vanillin and two methoxy groups in veratraldehyde. It is found that the condensations are progressively easier, quicker and more successful in the yields of the corresponding cinnamic acid derivatives.

The protocatechuicaldehyde gave 44% yield of caffeic acid, indicating that the steric hindrance is as powerful as it was in the isomeric 2 : 4-resorcylaldehyde, though in the present case none of the two hydroxy groups stands in the *ortho* position to the aldehyde group.

Vanillin, on the other hand, gave an appreciably higher yield of 51·5%, in a shorter time, *i.e.*, in 3·5 hours, of ferulic acid. And Veratraldehyde gave,

on two hours' heating, 57·6% and on a further two hours' heating, at a slightly higher temperature, 62·5% yields of dimethoxy-cinnamic acid.

The condensations in the above cases were brought about in the manner usual in the series, *viz.*, with the help of a trace of pyridine. Dutt on using the carbethoxy-derivatives of the first and the second had obtained, with the pyridine-piperidine mixture, only 7 and 12% yields respectively,[2] though, some years later, he obtained comparable yields by using quinoline in molecular proportions.[3]

The real progress in the case of these condensations is clearly demonstrated in the results obtained when the aldehydes were allowed to react alone with malonic acid without the presence of even a trace of a base or of any condensing agent. The three aldehydes in this case gave the following yields of the same acids, 16·6, 61·8 and 86·5 per cent. respectively and in a progressively shorter time (Table I). That the yields in the case of the last

TABLE I

	Molecular proportions			Temp.	Time	Yield %
	Alde.	Acid	Base			
Protocatechuic-aldehyde ..	1	1	0·15 pyridine	water-bath	5–6 hrs.	44·4
	,,	,,	,, ,,	,,	10 ,,	..
	,,	,,	,, ,,	,,	4 ,,	44·4
	1	1	0·0 no base	,,	5 ,,	16·6
Vanillin ..	1	1	0·15 pyridine	70°	3·5 ,,	51·5
	1	1	0·0 ,,	80°	,, ,,	61·8
Veratraldehyde ..	1	1	0·15 ,,	water-bath	2 ,,	57·6
	,,	,,	,, ,,	,, + 110°	,, ,, 2 ,,	62·5
	1	1	0·0 ,,	water-bath	3·6 ,,	86·5

two should have been higher in the absence than in the presence of a condensing agent is very striking.

Other condensing agents were tried in the case of protocatechuicaldehyde, in order to increase the yield if possible, *viz.*, piperdine, pyridine-piperidine mixture as used by Robinson and Shinoda[4], concentrated sulphuric acid, dry hydrogen chloride in the presence of absolute alcohol, etc., but the results

were disappointing. Hayduck has applied Stuart's method of using glacial acetic acid in place of a base[5] to protocatechuicaldehyde, and this method gave the yield of about 77%.

Recently Fritz Vorsatz[6] has reported an improvement in the synthesis of hydroxy-cinnamic acids. He employs the same materials in almost the same proportions as Robinson and Shinoda, *i.e.*, the aldehyde malonic acid, pyridine and piperdine in 1 : 2 : 6 : 0·1–0·2 mol. proportions, but instead of the high temperature of the latter, he keeps the mixture at room temperature, for three weeks. Knoevenagel had done this in several successful condensations and this principle of so to say substituting time in place of temperature has enabled Fritz Vorsatz to obtain almost record yields, *viz.*, 87% caffeic acid from photocatechuicaldehyde, 73% ferulic acid from vanilline and 83% of piperonylacrylic acid from piperonal.

Although 'the room temperature' is an exceedingly elastic phrase, and although the room temperature in Agra might hardly be comparable with the temperature of Vorsatz's rooms, experiments were tried on the same model here in Agra in the cold weather, and entirely confirmed his findings (Table II). Protocatechuicaldehyde gave as much as 83%, and vanillin 71·4% yield. The higher yield of the former seems to be anomalous and suggests as if the inhibitive effect of the hydroxy group underwent another modification at low temperatures. It has also to be observed that when

TABLE II

	Molecular proportions			Temp. approximately	Time	Yield %
	Alde.	Acid	Base			
Protocatechuicaldehyde ..	1	2	6 pyridine + piperidine trace	10°–25°	3 weeks	83·0
	,,	,,	,, ,, + ,,	25°–45°	3 months	46·1
	1	2	0·21 ,, + ,,	5°–20°	3 weeks	76·9
	1	2	0·21 pyridine	,,	,,	69·2
Vanillin ..	1	2	6 pyridine + piperidine trace	10°–25°	3 weeks	71·4
	1	2	0·39 ,, + ,,	25°–45°	3 months	62·0
	1	2	0·39 ,, + ,,	25°–20°	3 weeks	69·7
	1	2	0·39 pyridine	,,	,,	62·
Veratraldehyde ..	1	2	0·4 pyridine	,,	,,	81·7

the protocatechuicaldehyde mixture was kept for three months in the summer instead of three weeks in the winter, the yield was not further increased, but was, on the contrary, reduced to 46%.

Would the method of Vorsatz answer equally well when the bases were in traces only, or when there was only one base pyridine in a trace? This question has been faced and the answer is in the affirmative, the yields being almost the same, namely, about 77, 70 and 82% respectively from the three aldehydes. Further experimentation may assist in finding out conditions of better or theoretical yields, but as for practical purposes few would employ synthetic methods requiring three weeks or so, it is considered sufficiently satisfactory to note the efficiency of traces even in this method.

It may be observed that the complete suppression of the steric hindrance exercised by the two adjacent hydroxy-groups is demonstrated in the condensations of piperonal, wherein the two hydroxy groups are replaced by a methylene-dioxy-group and which has given almost quantitative yields.[7]

The nitro-group offers a kind of contrast to the hydroxy-, as the three nitro-benzaldehydes undergo the condensation easily and give very good yields of the corresponding nitro-cinnamic acids. These have been very well studied by a number of workers employing different methods. The pyridine-trace method has been recently applied by Rangaswami, Rao and Seshadri[8] to prepare *o*-nitro- and *m*-nitro-cinnamic acids. As they have not mentioned their yields, and as they did not study *p*-nitro-benzaldehyde, these are given below. It may be noted that here in each of the three cases the condensations proceed even when no base is present and the yields are, in the same period of time, over 50%.

Experimental

(With T. S. Sodhi)

The Condensation of Protocatechuicaldehyde and the Synthesis of Caffeic Acid.—2·7 g. Aldehyde, 2 g. malonic acid and 0·25 c.c. pyridine (1 : 1 : 0·15 mol.) were heated on a water-bath for 5–6 hours. The mass fused in 1·5 hours, then bubbling started, and then it gradually set to a solid. The product contained the unused aldehyde which was removed by refluxing with alcohol and animal charcoal. The caffeic acid so obtained weighed 1·6 g. (44·4%) and was of a light brown colour melting at 200°.

Longer heating gave a tarry mess, but the same yield was obtainable on 4 hours' heating. The yield diminished to 38·8% when the time of heating was reduced to 3 hours. When heated without a base 1·3 g. aldehyde gave

only 0·3 g. or 16·6% yield, which, however, gave a better melting-point (209°). When 0·15 mol. of piperidine was substituted, the yield was 16·6% on 5 hours' heating.

When a molecular quantity of pyridine was taken, or the still greater proportions according to Robinson and Shinoda (*loc. cit.*), a black resinous mass was obtained which yielded no caffeic acid.

Hayduck's Method.—3 g. Aldehyde, 3 g. malonic acid and 2 g. glacial acetic acid were heated on the water-bath for ten hours. The whole mass was a homogeneous liquid in half an hour and became brown in colour. Bubbles then came off. At the end the cooled mass was treated with water when an ash-coloured precipitate came down. It was filtered, and purified: it weighed 3 g. = 76·9% yield.

Vorsatz's Method.—2·5 g. Aldehyde, 3·85 g. malonic acid, 8·5 c.c. pyridine and 0·1 c.c. piperidine were kept in a loosely corked flask for three weeks at room temperature (ranging between 10° and 25° C. approximately). Water was then added and ammonium carbonate solution. The filtrate was acidified and extracted with ether. The ethereal extract when worked up gave 2·7 g. or 83% of caffeic acid.

Another flask containing the same mixture was left for three summer months, when the room temperature might have fluctuated between 25° and 45° C. The yield when worked up came only to 46%. But when instead of 6 mol. proportion of pyridine only 0·21 was taken, with or without additional trace of piperidine, the yields were quite good (*vide* Table II).

Condensation of Vanillin: Synthesis of Ferulic Acid.—3·1 g. Vanillin, 2·1 g. malonic acid, and 0·3 c.c. pyridine (1 : 1 : 0·15 mol.) heated at 70° for 3·5 hours gave 2 g. of ferulic acid, melting at 169°. The yield was poorer if higher temperatures were employed.

0·75 g. Vanillin, heated alone with 0·5 g. of malonic acid at 80° for 3·5 hours, gave 0·6 g. or 61·8%.

The yields obtained by Vorsatz method are given in the table.

Condensation of Veratraldehyde.—Veratraldehyde, obtained, by the methylation of vanillin, 1·6 g., malonic acid 1 g. and pyridine 0·12 c.c., on being heated on the water-bath for 2 hours, gave on being worked up in usual way, 1·2 g. (= 57·6% yield) of dimethoxycinnamic acid, m.p. 180°. When the heating was supplemented with another 2 hours' heating at 110°, the yield improved to 62·5%.

The same heated without pyridine, yielded 1·8 g. or 86·5%. Almost the same yield was obtained when the three, in 1 : 2 : 0·4 mol. proportions,

were kept for three weeks at room temperatures according to Vorsatz' method modified.

(With Dilbahar Singh Mittal)

Condensations of o-, m- *and* p-*Nitrobenzaldehydes.*—The procedure was exactly the same in the three cases : 1·5 g. of the aldehyde, 1·2 g. malonic acid and a trace of pyridine, (1 : 1 : 0·15 mol.) were heated on the water-bath for four hours. The three nitrocinnamic acids, taken out as usual, were all *trans*-nitrocinnamic acids and melted at 242·7° and 200° and 286° respectively. Piperidine and quinoline traces were also similarly employed and gave slightly lower yields. The reaction in each case went on also in the absence of any base, by heating the two together, and as judged from the yields in the same period of time, was half complete only.

TABLE III

Aldehyde	Molecular Proportions			Yield %
	Alde.	Acid	Base	
o-Nitrobenzaldehyde ..	1	1	0·15 pyridine	90·7
	,,	,,	,, piperidine	88·1
	,,	,,	,, quinoline	82·9
	1	1	0·0 no base	51·8
m-Nitrobenzaldehyde ..	1	1	0·15 pyridine	88·0
	,,	,,	,, piperidine	85·5
	,,	,,	,, quinoline	80·4
	1	1	0·0 no base	52·8
p-Nitrobenzaldehyde ..	1	1	0·15 pyridine	87·6
	,,	,,	,, piperidine	85·0
	,,	,,	,, quinoline	75·1
	1	1	0·0 no base	51·9

Summary

Condensations of protocatechuicaldehyde, vanillin and veratraldehyde with malonic acid in the presence of various proportions of bases, and in the absence of any base, show that the hydroxy-group generally diminishes the yield, which rises when the group is methylated. Influences of different proportions of the base, and of different temperatures and periods of time at

which the reactions are allowed to proceed are recorded. The trace of the base is generally as efficient as ever. The nitro-group on the other hand, when present on the nucleus, is not found to exert any restraining influence on the yields obtained, and allows very high yields of the nitro-cinnamic acids.

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SOME MEASUREMENTS OF CHLORIDE, NITRATE AND NITRITE PRESENT IN THE WATER OF THE MONSOON RAINS AT BOMBAY

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Introduction

Nuclei play a fundamental role in the condensation of water vapour in the atmosphere and it is obviously important to determine their amounts and distribution in the atmosphere in different parts of the world. Some of the primary processes taking place in the atmosphere, for example, the growth of rain-drops from cloud particles are still incompletely understood and it is probable that a study of the amounts of dissolved hygroscopic matter in different kinds of rain and in different parts of the country will throw light on the mechanism of rain-formation.

There are usually present in the atmosphere many kinds of condensation nuclei.[1] Apart from ions, the most important of them are :—

(1) Oceanic salts, mainly chlorides of sodium, calcium and magnesium.

(2) Nuclei formed by solar radiation or by electrical discharges in the atmosphere—ozone, oxides of nitrogen and perhaps also hydrogen peroxide.

(3) Nuclei raised from the ground by wind or generated in populated areas—such as silica, sulphur dioxide, soot, ammonia, etc.

It is also known that many kinds of soil when heated by insolation during day and cooled by radiation at night are capable of desorbing and absorbing moisture from the atmosphere.[2] Dust raised by wind from the soil and carried up by turbulence will also therefore contain particles of matter capable of acting as condensation nuclei in the atmosphere.

The following paper describes some measurements of the chloride, nitrate and nitrite contents of rain water collected at the Colaba Observatory, Bombay, during the monsoon season of 1938.

Collection and Analysis of Rain-Water

The samples of rain-water used for the analysis were collected at the top of one of the towers in the compound of the Colaba Observatory, Bombay, which is at a height of about 70 ft. above ground and 100 ft. above mean sea-level.

The Observatory being situated in the extreme south of Bombay City and at a distance of more than four miles from its busy portions, there is not much road traffic in its neighbourhood and with a prevailing westerly to south-westerly wind the samples of water collected may be considered to be unaffected by artificial contamination. Even then, the samples showed the presence of some insoluble particles, but the amount was too small to be estimated by their dry weight. The water was received in a well-cleaned glass funnel and collected in a pyrex flask with a long narrow neck, from which it was transferred to chemically cleaned Jena glass bottles. If the rain occurred in spells with intervals of rainless weather, the bottle was kept closed during intervals. Estimations of the chloride, nitrate and nitrite content were made soon after a sufficient quantity had been collected for the analysis.

For preparing the reagent solutions for the analysis, chemicals of the purest variety, either Merck's or Kahlbaum's A.R. quality, were used. The glass distilled water was tested and found free from chloride, nitrate and nitrite and it was further boiled and preserved cool in glass-stoppered pyrex flasks.

The concentrations of the chlorides, nitrate and nitrite radicals were determined colorimetrically ; the solutions were kept in Nessler tubes in a small camera box similar to that described by Mason and Buswell[3] in their book on *Examination of Water* (sixth edition) and the colours compared visually.

For the estimate of the chloride radicals, a known quantity of the sample of rain-water was titrated against a standard solution of silver nitrate using potassium chromate as indicator. The sodium chloride solution used for standardising the silver nitrate solution[4] contained 0·05 mg. of chloride per c.c. The nitrite was estimated colorimetrically by the addition of sulphanilic acid and α-naphthylamine acetate solution to the sample. The final standard solution of sodium nitrite was so adjusted that 1 c.c. contained 0·0005 milligrammes of nitrogen or 0·00164 mg. of NO_2. For estimating the nitrate radical, the nitrite was first eliminated by the urea method[5] and the determination of the nitrate was carried out by the Phenol-di-sulphonic acid method.[6] The phenol-di-sulphonic acid reagent was prepared by the method described by Grandval and Lajowx.[7] The standard potassium nitrate solution contained 0·01 mg. of N or 0·0443 mg. of NO_3 per c.c. A known volume of the sample of rain-water was concentrated to dryness by evaporation and after cooling, phenol-di-sulphonic acid was gradually added. The mixture was diluted with distilled water and a strong solution of potassium hydroxide was added slowly until the maximum colour was developed. The different samples of rain-water were intercompared after the development of colour reactions.

The results of the analysis are shown in Table I.

TABLE I

Amounts of chloride, nitrate and nitrite in rain-water collected at Bombay

(Milligrammes per litre)

Date	Time	Amount of rainfall	Remarks about wind, nature of rain, etc.	Amount of chloride	Amount of N as NO_3	Amount of N as nitrite
13—6—1938	12 hrs.	0″·6	Strong, gusty wind—S.W. to W. —continuous rain for nearly four hours	22·3	Not determined	Not determined
14—6—1938	16 hrs.	3″·2	Strong, gusty wind—S.W. to W. —thunder and lightning long continued rain	16·0	0·24	0·0008
15—6—1938 to 22—6—1938	7 days	1″·1	Light occasional showers and one moderately good rain (on the 18th)—wind moderate—10–15 m.p.h. Heavy rain	13·3	0·14	0·0005
22—6—1938 to 23—6—1938	2 days	2″·3	Most of the rain fell between 5½ and 10 hrs. on the 23rd. Wind was weak with a few light squalls	6·5	0·12	0·0004
26—6—1938 to 28—6—1938	3 days	0″·8	Strong, gusty wind (15-20 m.p.h.). Rain mainly in intermittent showers and continuous light rain.	17·0	0·14	Very small
1—7—1938 to 3—7—1938	3 days	1″·5	Showers, continuous light rain and one spell of heavy rain when wind was very weak	26·0	0·12	Very small
4—7—1938 to 12—7—1938	8 days	6″·0	A good deal of continuous light rain with occasional showers from the 6th and strong and very gusty winds on the 10th, 11th and 12th	26·5	0·10	Very small
14—7—1938 to 20—7—1938	6 days	2″·0	Most of the rain fell in long continued spells on the 16th, 17th and 18th—gusty squally wind	17·8	0·10	0·0003
7—8—1938	15 hrs.	3″·2	Intermittent heavy rain—weak wind	2·7	0·14	0·0004
7—8—1938 to 8—8—1938	16 hrs.	1″·1	Continuous rain. Wind of low speed	4·7	0·12	0·0004
10—8—1938 to 11—8—1938	12 hrs.	0″·4	Thunderstorm rain	7·0	0·18	0·0008
14—9—1938	14 hrs.	7″·0	Very weak wind. Heavy rain with mild thunder	4·5	0·12	0·0004

TABLE I—(*contd.*)

Date	Time	Amount of rainfall	Remarks about wind, nature of rain, etc.	Amount of chloride	Amount of N as NO_3	Amount of N as nitrite
30—9—1938 to 1—10—1938	14 hrs.	3″·5	Strong thunder and lightning, but low wind	7·5	0·18	0·0020
2—10—1938 to 4—10—1938	2 days	3″·6	Continuous light rain and occasional showers. Thunder and lightning. Depression near Bombay.	17·5	0·08	0·0004
5—10—1938 to 6—10—1938	2 days	6″·9	Depression near Bombay. Very high wind and continuous rain	14·7	0·08	0·0004
			Mean ..	13·6	0·133	·00062

The results given in the above table show that in general, the rain-water collected at the time of thundershowers contains more nitrate and nitrite than at other times. It also appears that the relative excess of nitrite during thunderstorms is greater than that of nitrate. The amount of nitrogen combined as nitrite is much smaller than that as nitrate. The chloride content does not appear to be affected by thunder and lightning, but it is generally smaller in heavy rains than in light rain or drizzle. This is probably due to the smaller size and the relatively larger number of drops and nuclei brought down by drizzle than by heavy rain. The chloride content is also smaller when there is little wind than when there is a strong wind. The fact that Bombay is on the seacoast and that at times of strong wind, an appreciable amount of sea-spray gets mixed up with the rain is no doubt mainly responsible for this.

Comparison of the salt contents of rain-water in Bombay with those observed in other places.

At Bombay during the monsoon the chlorine content of rain-water varied in amount from 2·7 parts to 26·5 parts per million, the nitrate nitrogen from 0·08 to 0·24 and nitrite nitrogen from hardly measurable quantities to 0·0020 parts per million. It is of interest to compare these amounts with those observed in other places.

In India itself some observations have been made by J. W. Leather at Cawnpore and Dehra Dun on the nitorgen content of rain-water. A paper by N. H. J. Miller in *the Journal of Agricultural Science*, 1905–6, **1**, summarises a large amount of data obtained in different parts of the world.

Table II gives a summary of representative observations from different countries.

TABLE II

(a) Chlorine-content of rain-water

(In milligrammes per litre)

Place	Amount of chlorine			Remarks	Authority
	Mean	Maximum	Minimum		
England, Rothamsted	2·3	20·1	0·40	..	N. H. J. Miller[8]
England, Cirencester ..	3·2	10·4	1·15	..	E. Kinch[9]
England, Towns ..	8·4	25·0	1·2	..	R. Angus Smith[10]
Scotland, Sea coast country places ..	12·1	49·0	1·2	..	do.
Scotland, inland country places	3·3	5·4	1·8	..	do.
Ireland, Valencia ..	47·0	..	..	..	do.
U.S.A. Troy, N.Y. ..	1·6	3·0	0·3	Rain and melted snow (monthly means)	Mason and Buswell[3]
U.S.A. Washington D.C.	1·3	3·0	..	23 samples collected in 1923-24	H. B. Riffenburg[11]
U.S.A. Blacksburg (Virginia) ..	0·23	0·4	0·05	..	do.
U.S.A. Mt. Vernon Iowa	3·5	28·1	..	Samples collected in 1922-23	Woehlk[12]
German specimens ..	1·3	..	..	..	R. Angus Smith
Scandinavia	3·5	..	..	Hoarfrost from fog at the Haldde Observatory	H. Kohler[13]
India, Calcutta ..	3·2	5·4	1·8	..	N. H. J. Miller
Ceylon	9·7	..	..	..	do.
India, Bombay ..	13·6	26·5	2·7	Mainly monsoon rain	R. Narayanaswami

(*b*) *Nitrate content of rain-water*

(In milligrammes of nitrogen per litre)

Place	Amount			Remarks	Authority
	Mean	Maximum	Minimum		
England, Rothamsted	0·18	2·16	0·09	Data refer to monthly samples in thirteen years	N. H. J. Miller
England, inland country places	0·17	0·41	0·11	..	R. Angus Smith
England, Town ..	0·19	0·31	0·06	..	do.
Scotland, inland country places	0·068	0·24	0·002	..	do.
Scotland, sea coast country places	0·094	0·20	0·005	..	do.
German specimens ..	0·64	..	..	..	do.
France, Paris ..	0·73	..	..	..	do.
U.S.A. Mt. Vernon ..	0·35	..	..	..	Weehlk
Dehra Dun	0·07	..	..	..	J. W. Leather[14]
Cawnpore	0·069	..	..	..	do.
Calcutta (1891) ..	0·115	..	..	..	N. H. J. Miller
Ceylon (1898-99) ..	0·069	..	..	..	do.
E. Java (1891) ..	0·011	..	..	..	do.
Pretoria	0·196	..	..	Weekly samples (1904–05)	H. Ingle[15]
Bombay	0·13	0·24	0·08	Mainly monsoon rains	R. Narayanaswami

(*c*) *Nitrite content of rain-water*

((in milligrammes of nitrogen per litre)

Place	Amount			Remarks	Authority
	Mean	Maximum	Minimum		
Switzerland, St. Chamas	0·133	0·316	0·0	..	N. H. J. Miller
Sicily, Catania ..	0·0006	·0027	0·0001	..	do.
Russia, Ploty ..	0·011	·025	0·0	..	do.
Bombay	·0006	·002	0·0	Mainly monsoon rain	R. Narayanaswami

The chloride concentrations vary enormously, being as much as 47 parts per million on the west coast of Ireland and as small as 0·23 in the interior of the United States. The Bombay values are comparable with those observed in Ceylon and in sea coast country places in Scotland. The nitrate nitrogen content observed at Bombay is nearly the same as those observed in Calcutta, but larger than those observed by Leather in the United Provinces. There do not seem to be many observations of nitrite nitrogen ; but the amounts observed at Bombay are about the same as those observed in Catania in Sicily. On the whole the amounts of chloride and nitrogen oxides in a tropical place like Bombay are of the same order of magnitude as those observed in countries of higher latitude.

In countries of temperate latitudes where westerly upper winds prevail, the chloride content seems to decrease with increasing distance from the west coast of the continent until we approach the east coast. This agrees with the idea that the sea is the main source of the chlorides. The mean chloride content of rain water at Bombay is larger than normal and it would be of interest to have further observations on the chloride content of rain-water at a few selected stations, both high level and low level, in different parts of India.

The above study was carried out at the suggestion of Dr. K. R. Ramanathan, and I am thankful to him for his kind interest in the work.

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THE QUESTION OF THE FIXATION OF THE AROMATIC DOUBLE BONDS IN HYDROXY-CHROMONES AND COUMARINS. FORMATION OF AZO-DYES

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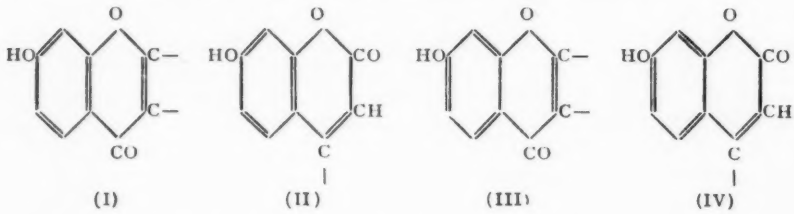
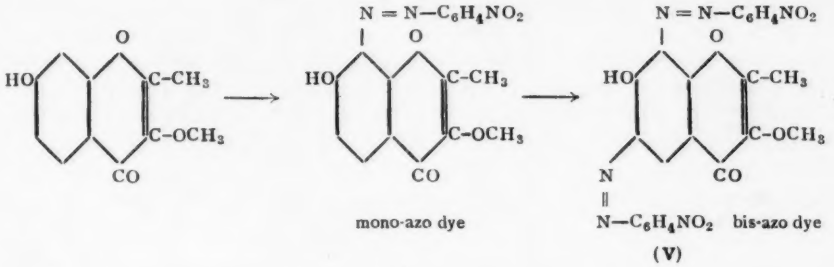
From a detailed study of the properties of 7-hydroxy-chromones and coumarins with particulr reference to the possibility of the fixation of the aromatic double bonds it was concluded that no rigid fixation exists.[1, 2] It is true that the eighth position is predominantly reactive indicating a possible fixation of the aromatic double bonds as in (I) and (II) but the other alternatives (III) and (IV) promoting reactivity of position six do not seem to be altogether prohibited. It was noticed that when a fresh pyrone ring was sought to be introduced umbelliferone gave rise to two isomeric (7 : 8-) and (7 : 6-) compounds, the former being produced in a predominant proportion.[3] In regard to Fries migration, allyl transformation and azo-dye formation, though position 8 is the one to react first, when it is protected by alkyl or allyl groups position six also exhibits reactivity.



Coupling with diazonium salts to form azo-dyes is a very facile reaction taking place energetically even at low temperatures. As a consequence of the results summed up in the above paragraph it was expected that when 7-hydroxy-chromones and coumarins were treated with diazonium salts bis-azo dyes would be produced due to reaction at the eighth and sixth positions in quick succession (V). As a matter of fact our early experiments carried out two years ago supported this expectation. In the meantime a paper

by Mahal and Venkataraman[4] recorded that 6-hydroxyflavone forms only a mono-azo dye and the authors comparing this result with the observations



(V)

of Perkin[5] who obtained bis-azo dyes from chrysin, apigenin, etc., expressed the opinion that this difference should be attributed to the existence of the fixation of the aromatic double bonds in the hydroxyflavones as in (I). The effect of this fixation should be the same whether the hydroxyl group is in the sixth or the seventh position so that 6-hydroxy-and 7-hydroxyflavones should behave alike. It was therefore felt necessary to examine in detail the behaviour of 7-hydroxy-chromones and coumarins in regard to the formation of azo-dyes. The following hydroxy-benzopyrones have been studied : (i) 2-methyl-3-methoxy-7-hydroxychromone, (2) 7-hydroxy-flavone, (3) 7-hydroxycoumarin (umbelliferone) and (4) 4-methyl-7-hydroxycoumarin. In one series of experiments one molecular proportion of diazotised *p*-nitraniline has been employed and in another more than two molecular proportions. The products have been characterised by the melting point and nitrogen content and the results are presented in the form of a table.

In the case of (I) there is considerable formation of the bis-azo dye even when one molecular proportion of the diazonium salt is employed. With more than two molecular proportions the formation of the bis-azo dye is complete. On the other hand in the case of the hydroxyflavone (II) the mono-azo dye is obtained pure when one molecular proportion is employed and with a large excess of the diazonium salt only a small quantity of the bis-azo dye is produced along with a large amount of the mono-azo compound which is still the main component.

In the case of the coumarins when caustic soda is employed the formation of the bis-azo dye takes place very easily even with one molecular proportion of the diazonium salt obviously due to the fact that the α-pyrone ring has been opened out by the caustic akali. When this is prevented by using aqueous sodium carbonate mono-azo dyes alone are produced with one

Phenolic compound	Medium	No. of molr. proportions of diazotised nitraniline used	M.P.	% N found	% N Calc. for		Colour of the dye
					mono-azo dye	bis-azo dye	
I. 2-Me-3-MeO-7-hydroxy-chromone	Sodium hydroxide	1	> 360°	14·9	11·8	16·7	Deep violet
,,	,,	> 2	,,	16·8			,,
II. 7-Hydroxy-flavone	,,	1	300° (d.)	10·9	10·9	15·7	Deep reddish brown
,,	,,	> 2	260–300° (d.)	12·2			,,
III. 7-Hydroxy-coumarin	Sodium carbonate	1	283° (d.)	13·7	13·5	18·3	Deep brown
,,	,,	> 2	210–276° (d.)	15·3			,,
IV. 4-Methyl-7-hydroxy-coumarin	,,	1	251–252° (d.)	12·9	12·9	17·7	Brown
,,	,,	> 2	210–250° (d.)	13·7			,,
V. ,,	Sodium hydroxide	1	220° (d.)	17·4	12·9	17·7	Pink brown
,,	,,	> 2	,,	17·7			,,

molecular proportion of the diazonium salt and with a large excess of the reagent only a partial formation of the bis-azo dyes takes place. The coumarins therefore behave like 7-hydroxy-flavone.

It is therefore clear that though in all cases the formation of the bis-azo dyes is possible it seems to take place with difficulty in a large number of examples. Our results recorded above indicate that they are formed in appreciable quantities though their isolation in the pure state has been possible in only one case. These are in support of the conclusion already expressed in our previous publications that the fixation of the aromatic double bonds in the benzo-pyrones is not a very rigid one. Further the composition of the dyes produced is obviously not controlled by the fixation of the double bonds, at any rate not entirely, and seems to depend on various other factors such as the reactivity of the components, the solubility of the mono-azo dye that may first be produced and its capacity to react further to form the bis-azo dye.

Experimental

The reactions were carried out under carefully controlled and standardised conditions so that the results obtained might be comparable. The following paragraph describes a typical experiment.

8-p-Nitrophenylazo-7-hydroxycoumarin—

p-Nitraniline (2 g.) was dissolved in 50% hydrochloric acid (15 c.c.) and the solution after being cooled to 0° was treated in drops with an ice-cold solution of sodium nitrite (1·5 g. in 10 c.c. of water), the temperature being kept below 5° throughout the addition. The diazotised solution was then diluted to 50 c.c. using ice-cold water.

7-Hydroxycoumarin (0·7 g.) was dissolved in 10% aqueous sodium carbonate (60 c.c.) and treated with sodium acetate (6 g. dissolved in 20 c.c. of water) and then with the solution of the diazotised amine (16 c.c.—one molecular proportion) which was added slowly with stirring, the temperature not being allowed to exceed 5°. The mixture was well shaken and then left in in the ice-chest. The dye separated at the top as a foamy mass in the course of half-an-hour. After keeping for two days in the ice-chest during which period it was shaken now and then the solid was filtered with suction, drained well and crystallised from hot glacial acetic acid in which it was fairly soluble. Another crystallisation from the same solvent gave the dye in the form of a deep brown powder which had the appearance of small prisms under the microscope. It was then washed with a large volume of water and then with a little alcohol. The yield was almost quantitative.

In the case of the chromones a corresponding amount of sodium hydroxide was used. When the product could not be dissolved in hot acetic acid, purification was effected by boiling it twice with a large excess of the solvent and filtering hot. The yields were uniformly good, varying from 70–90% of the theoretical.

Summary

The formation of azo-dyes using one and more than two molecular proportions of diazotised *p*-nitraniline and the following compounds has been investigated: (i) 2-methyl-3-methoxy-7-hydroxychromone, (2) 7-hydroxyflavone, (3) 7-hydroxycoumarin and (4) 4-methyl-7-hydroxycoumarin. (I) yielded a bis-azo dye with two molecules of the reagent and with one molecule of it a large proportion of the same bis-azo dye contaminated with the mono-azo compound. The other three behaved alike yielding mono-azo dyes with one molecule of the reagent and the same mono-azo compound predominantly mixed with considerable amounts of the bis-compounds when

more than two molecular proportions of the reagent were employed. The factors controlling the composition of the azo-dyes that are formed seem to be very complex.

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THE 7-15 PROBLEM

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The general problem namely, whether it is possible to invite $2n + 1$ people to dinner at a round table on n days so that no two people come together on more than one day, is still unsolved. The case when $2n + 1$ is a prime is trivial. Recently Dr. Chowla* and others showed that the arrangement is possible when n is equal to 4 and 10. The problem has therefore been solved for all values of n from 1 to 10 with the exception of 7. The aim of this paper is to fill up this gap for $n = 7$. The different arrangements in this case are given below.

(1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15)
(1, 3, 5, 7, 9, 11, 13, 15, 2, 4, 6, 8, 10, 12, 14)
(1, 4, 7, 10, 13, 2, 5, 8, 11, 14, 3, 6, 9, 15, 12)
(1, 5, 9, 13, 3, 7, 11, 15, 4, 8, 12, 2, 6, 14, 10)
(1, 6, 15, 10, 5, 14, 9, 4, 13, 8, 3, 12, 7, 2, 11)
(1, 7, 15, 8, 14, 2, 10, 4, 12, 6, 13, 5, 11, 3, 9)
(1, 8, 2, 9, 12, 5, 15, 3, 10, 6, 11, 4, 14, 7, 13)

Note added in Proof :—This solution was obtained independently of and communicated before the publication of the recent papers by Gupta (*Proc. Ind. Acad. Sci.*, 1939, **9**, 399) and Chowla (*Proc. Ind. Acad. Sci.*, 1939, **9**, 419). The problem has been solved by them and Prof. Levi appears to have obtained a solution for all n. Nevertheless, the solution given here is a different one from that given in Gupta's paper for $n = 7$.

* *Proc. Ind. Acad. Sci.*, 1939, **9**, 103.

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